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16. ABSTRACT

Secondary ion mass spectrometry is evaluated for application to the determination of the composition and structure of individual particles. Analyses of many elemental constituents at the ppm level can be obtained in individual particles as small as 2μm in diameter. Molecular signals, both organic and inorganic, can be detected from particles above 20μm in diameter. Quantitative analyses of elemental constituents can be made with a relative accuracy of 25 percent by means of empirical relative sensitivity factors and within a factor of two by means of a physical model. Multi-element depth profiles can be obtained from individual particles as small as 4μm in diameter. Depth profiles of individual particles from SRM 1648 Urban Air Particulate reveal pronounced surface concentrations of lead and barium. Implementation of SIMS depth profiling requires automation to make use of the full spectral information and to eliminate matrix effects by normalization.

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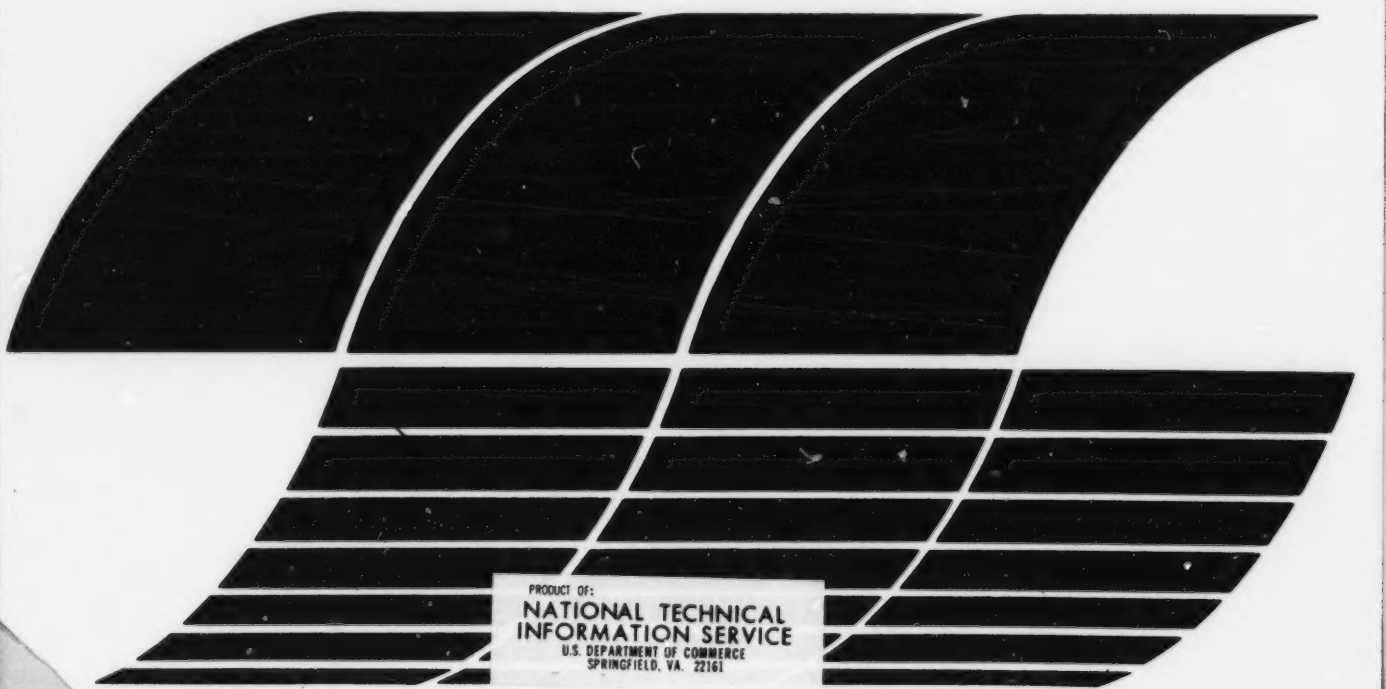
Interagency Energy/Environment R&D Program Report



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MICROANALYSIS OF INDIVIDUAL LAYERED PARTICLES BY SECONDARY ION MASS SPECTROMETRY

by

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Interagency Energy/Environment R and D Program Report

DISCLAIMER

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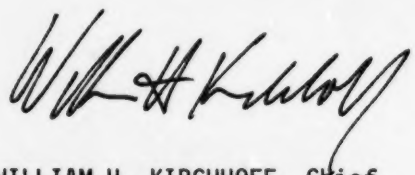
FOREWORD

The role of the National Bureau of Standards in the Interagency Energy/Environment R&D Program, coordinated by the Office of Research and Development of the U. S. Environmental Protection Agency, is to provide those services necessary to assure data quality in measurements being made by the Federal, state, local, and industrial laboratories participating in the interagency program. The work at NBS is coordinated by the Office of Environmental Measurements and is conducted in the Center for Analytical Chemistry, the Center for Radiation Research, and the Center for Thermodynamics and Molecular Science. NBS activities form part of the Characterization, Measurement, and Monitoring Program Category and address the data quality assurance needs of air and water monitoring programs. NBS efforts in support of data quality assurance include:

- Studies of the feasibility of production of Standard Reference Materials which could be used for the verification of performance audit samples for quality control programs or used for the calibration of field and laboratory instruments.
- The development and demonstration of new or improved measurement methods, particularly when needed for the certification of Standard Reference Materials.
- The evaluation and dissemination of data on the physical and chemical properties of effluents, products and raw materials of environmental significance in energy production.
- The provision of reference materials for the evaluation and validation of monitoring methods.

This report is one of the Interagency Energy/Environment Research and Development Series Reports prepared to provide detailed information on the development of an NBS measurement standard or method.



WILLIAM H. KIRCHHOFF, Chief
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ABSTRACT

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1. INTRODUCTION

When a particulate sample is examined by an analytical technique which is capable of characterizing individual particles, we frequently observe that the sample is inhomogeneous on the scale of the individual particles, even when major elements are considered. It is often of considerable value in identifying the origin(s) of a particulate sample to have knowledge of the types of individual particles which make up the sample and their frequency. The highly developed and widely used technique of electron probe microanalysis is capable of characterizing major and minor elements at a concentration greater than 0.1% and with an atomic number of 11 or more in individual particles. Once we are capable of assessing variations in composition between individual particles, the next level of interest becomes the study of structure which may exist within an individual particle. Electron probe microanalysis can characterize local inhomogeneities, but the spatial resolution is limited by the finite size of the electron interaction region, which has a volume of about 1 μm^3. Studies with the electron probe frequently reveal that individual particles have complex variations in composition on this scale. However, because of the penetration of the electrons into the solid, to a range of 1 μm or more, it is not possible to study compositional variations along the depth axis of individual particles.

In recent years, the technique of secondary ion mass spectrometry (SIMS) has been developed, offering a number of interesting advantages to the study of particles (1,2,3). In the SIMS technique, a beam of energetic ions is used to sputter atoms from a target. During the sputtering process a fraction of the atoms knocked from the target is emitted in a charged state, the so-called secondary ions. These secondary ions are analyzed within a mass spectrometer, producing a mass spectrum of a small volume of the target. Because it is a mass spectrometric technique, SIMS is capable of detecting all elements in a target. Molecular species can also be detected in SIMS spectra, including complex organic compounds. Isotopic ratios can also be measured.

The lateral resolution of the ion microprobe, a focussed beam SIMS instrument, is of the order of 1 μm, which is similar to that of the electron microprobe. However, the depth resolution of a SIMS instrument is much better than that of the electron microprobe. Secondary ions are emitted from a region of the sample which lies with 1 - 2 nm of the sample surface, which is about one percent of the sampling depth of x-rays in electron probe microanalysis. The sputtering process which forms the basis of SIMS provides a means by which the sample can be eroded in a controlled fashion. Thus, in a layered sample, the structure perpendicular to the surface can be exposed in a sequential fashion. Coupled with the shallow sampling depth of the

secondary ions, SIMS can provide an elegant technique for the characterization of particles both laterally and in depth.

In order to successfully apply SIMS to the study of particles, this study addressed three problems. (1) Quantitative analysis by SIMS is complicated by the existence of strong matrix effects on secondary ion signals. In order to establish a quantitative basis for SIMS analysis, an extensive study was conducted on empirical and theoretical models for the interpretation of the SIMS spectra. This study is reported in Section 2 of this report. (2) Particles of a non-conducting nature represent a difficult target for charged-beam analysis techniques. Methods were developed for the mounting and analysis of individual particles (Section 3). (3) SIMS spectra frequently contain signals which are related to inorganic and organic molecular fragments. A study was conducted to assess the utility of the ion microprobe, a high current density SIMS instrument, for the detection of characteristic signals from various compounds when the target is in the form of small particles (Section 4). Finally, based upon these studies, a number of particles taken from samples of environmental interest have been examined by SIMS (Section 5).

2. CONCLUSIONS

This study has demonstrated that:

(1) High sensitivity mass spectrometry can be successfully carried out on individual environmental particulates with a size below 10 μm, even if these particles have an insulating character.

(2) Molecular signals, both inorganic and organic, can be detected at intermediate ion beam current densities appropriate to the measurement of particles as small as 20 μm.

(3) Quantitative analyses can be performed with relative sensitivity factors with a relative accuracy of 25 percent in a majority of cases. Physical models of ion emission can yield relative accuracies of a factor of two or better in a majority of cases.

(4) Sensitivities in the ppm range can be obtained for many elements in a silicate matrix when the sample is in the form of a particle of 2 μm or larger.

(5) Multi-element depth profiles can be successfully obtained from individual particles as small as 4 μm in size. Depth resolutions of 100 nm or better are possible on particles.

(6) In SRM 1648 Urban Air Particulate, depth profiling reveals that heavy metals such as lead and barium are predominantly concentrated at the surface of the particles, with the surface concentration as much as 100 times greater than the interior.

(7) Practical implementation of the SIMS depth profiling technique to individual particles requires an automated instrument to make full use of the multi-element characterization capability and to maximize the depth resolution.

3. METHODS FOR QUANTITATIVE ANALYSIS IN SECONDARY ION MASS SPECTROMETRY

INTRODUCTION

In performing chemical analysis for the elemental constituents of a sample by SIMS, it is necessary to relate the measured secondary ion intensities detected from the sputtered assemblage to the atom concentrations in the original, undisturbed material. The analytical methods by which the composition can be calculated from the spectral data include a variety of empirical and theoretical approaches (4). To appreciate the magnitude of the calculational problem, it is useful to consider the various factors which influence the measured secondary ion intensities: (1) Matrix effects--the sputtering process is illustrated schematically in Figure 1. The secondary ion fraction of the sputtered atoms is small, typically in the range 10^{-3} - 10^{-1}. Atomic ions, $M^{\pm}$, are the predominant species observed in the secondary ion fraction for light elements (Z<40); cluster ions, $M_n^{\pm}$, and molecular ions, $M_x O_y^{\pm}$, are also observed (Figure 2 and Figure 3). In the case of bombardment of a heavy element with a reactive primary ion such as oxygen, the molecular ions tend to dominate the atomic ions by a factor of 10 or more.

The normalized positive secondary ion yield observed from the pure chemical elements, Figure 4, shows a variation of more than four orders of magnitude across the periodic table, approximately related to the reactivity of the individual elements with oxygen (5). When an electropositive primary ion such as cesium is used and negative secondary ions are measured, a similar strong variation in the normalized secondary ion intensity is observed, with the sensitivity related to the electron affinity (4). These extraordinary variations in the sensitivity are believed to occur as a result of differences in the availability of electrons in the surface region from which the secondary ions are ejected. Free electrons act to modulate the processes of neutralization or electron capture (6). Thus, variations in the electronic character of the surface can lead to pronounced matrix effects. The presence of adsorbed reactive gas species, the accumulation of the implanted primary ion species, as well as the basic characteristics of the bulk matrix species can influence the surface electronic character. Moreover, the nature of the surface region can change during the course of a SIMS experiment due to sputter-induced variations in the adsorbed oxygen on the surface and the time dependent build-up of the implanted primary ion species. Thus, the SIMS signal is subject to time-varying effects. (2) Instrumental effects--the extremely strong matrix effects noted above have tended to overshadow the

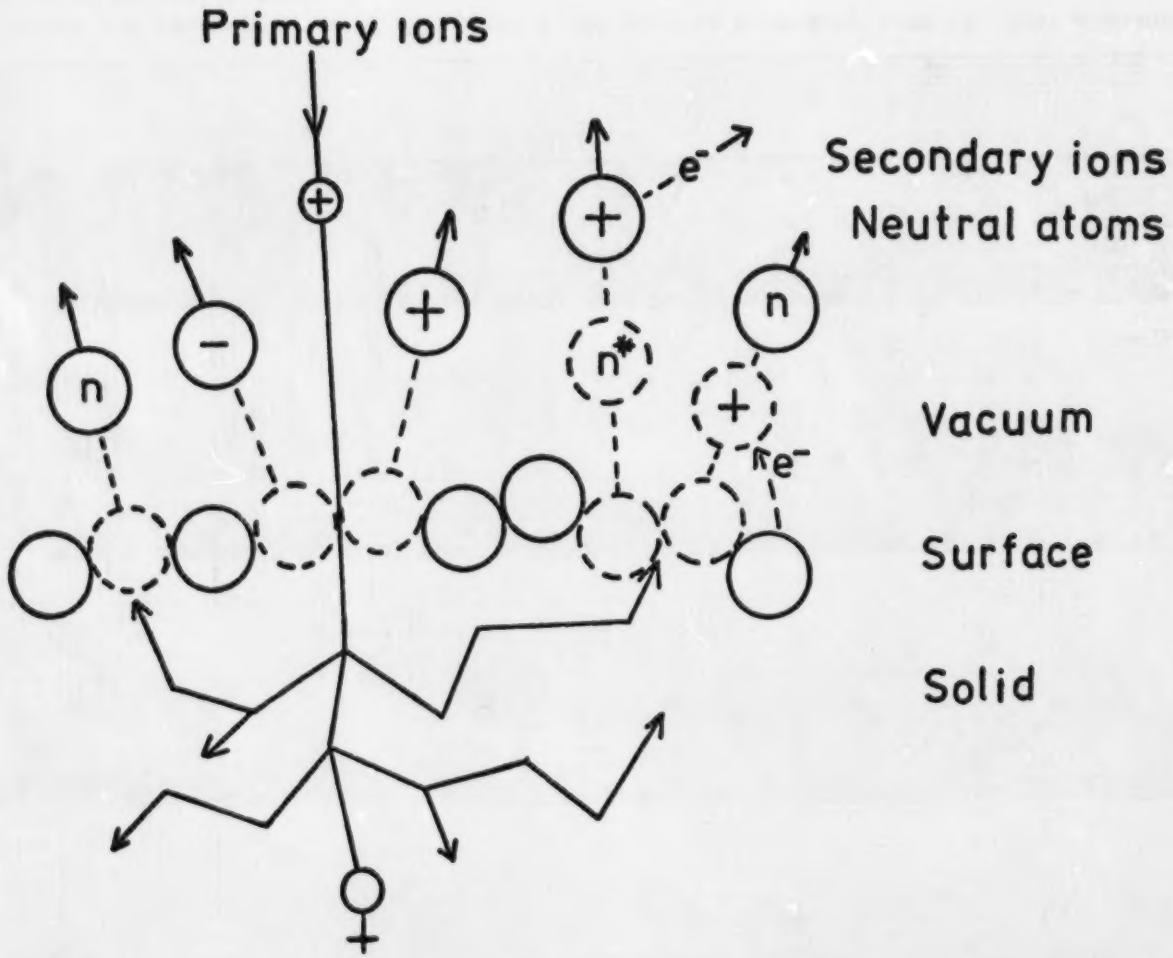

Figure 1. Schematic illustration of the sputtering process, illustrating secondary ion emission and neutralization processes.

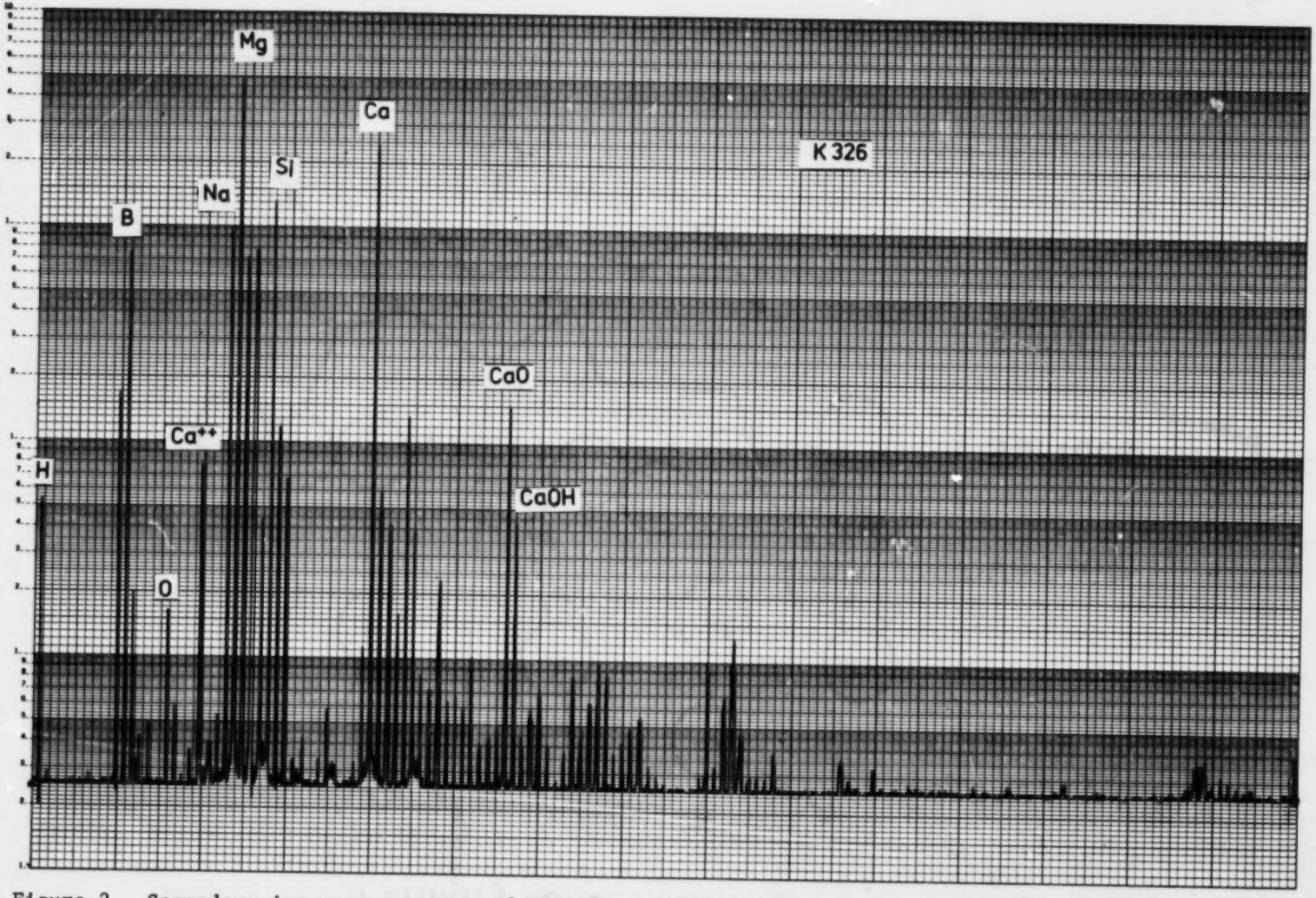

Figure 2. Secondary ion mass spectrum of NBS glass K 326 showing secondary ions of light elements, and associated molecular ions.

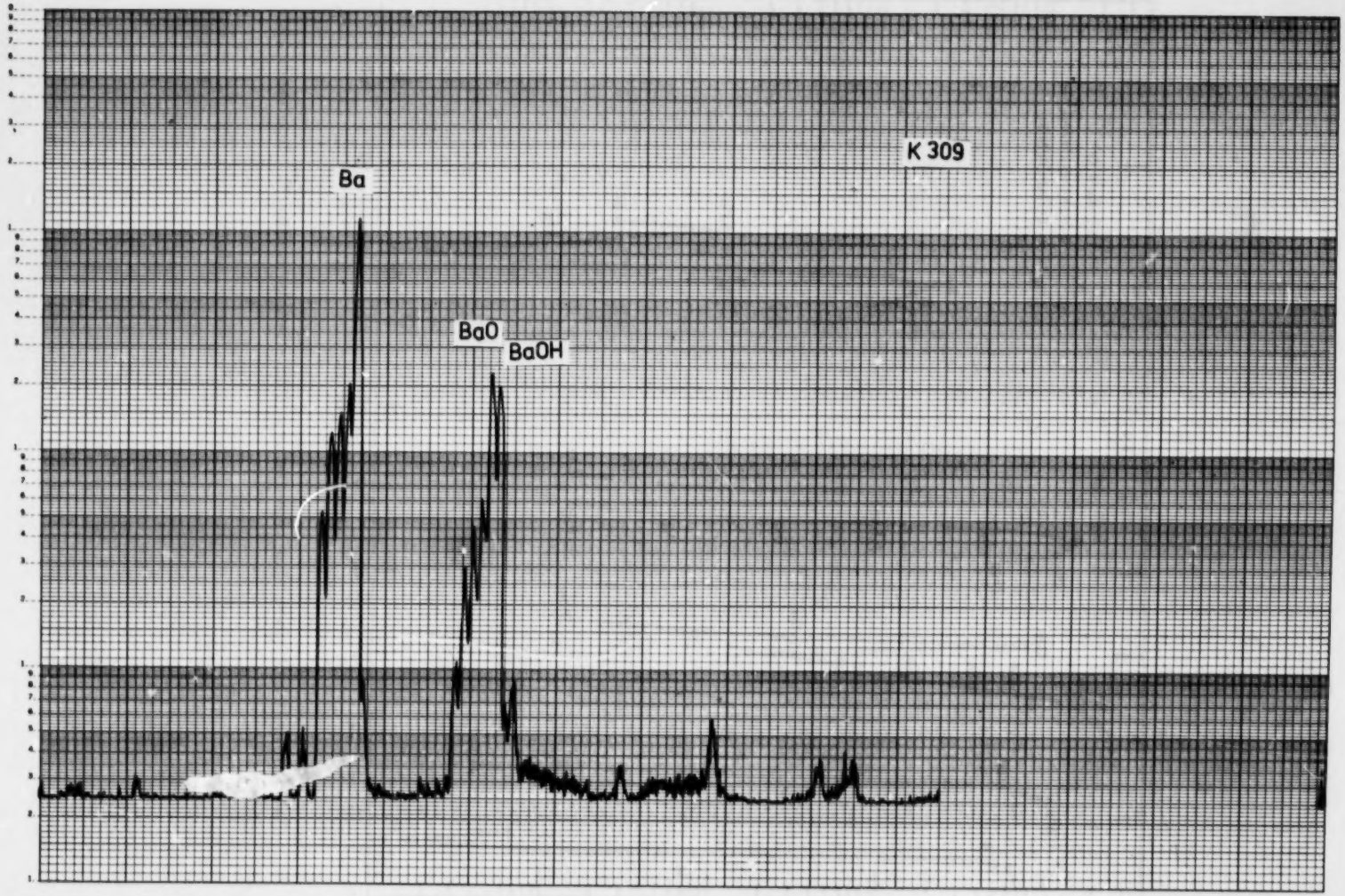

Figure 3. Secondary ion mass spectrum of NBS glass K 309 showing secondary ions of an intermediate mass species, barium, and the associated oxide and hydroxide ions.

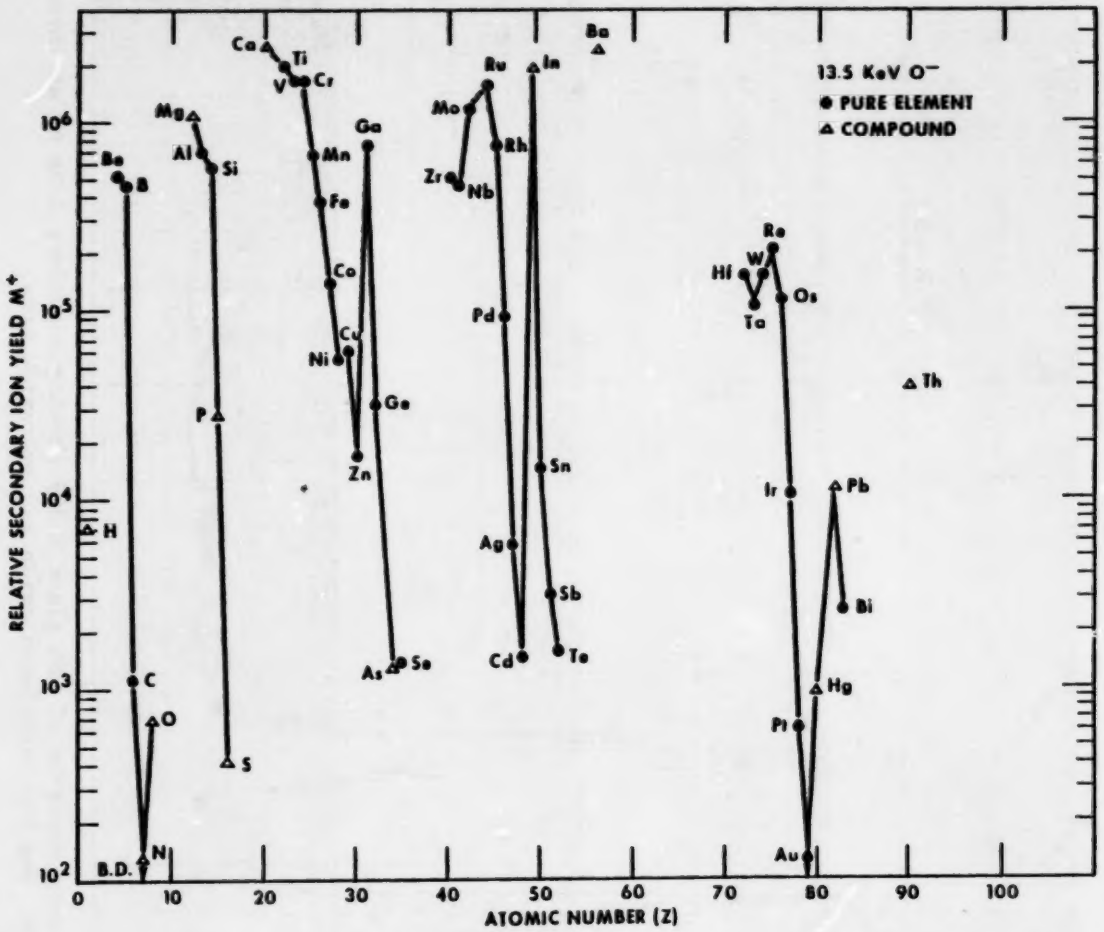

Figure 4. (a) Normalized positive secondary ion yields under O^- bombardment (5).

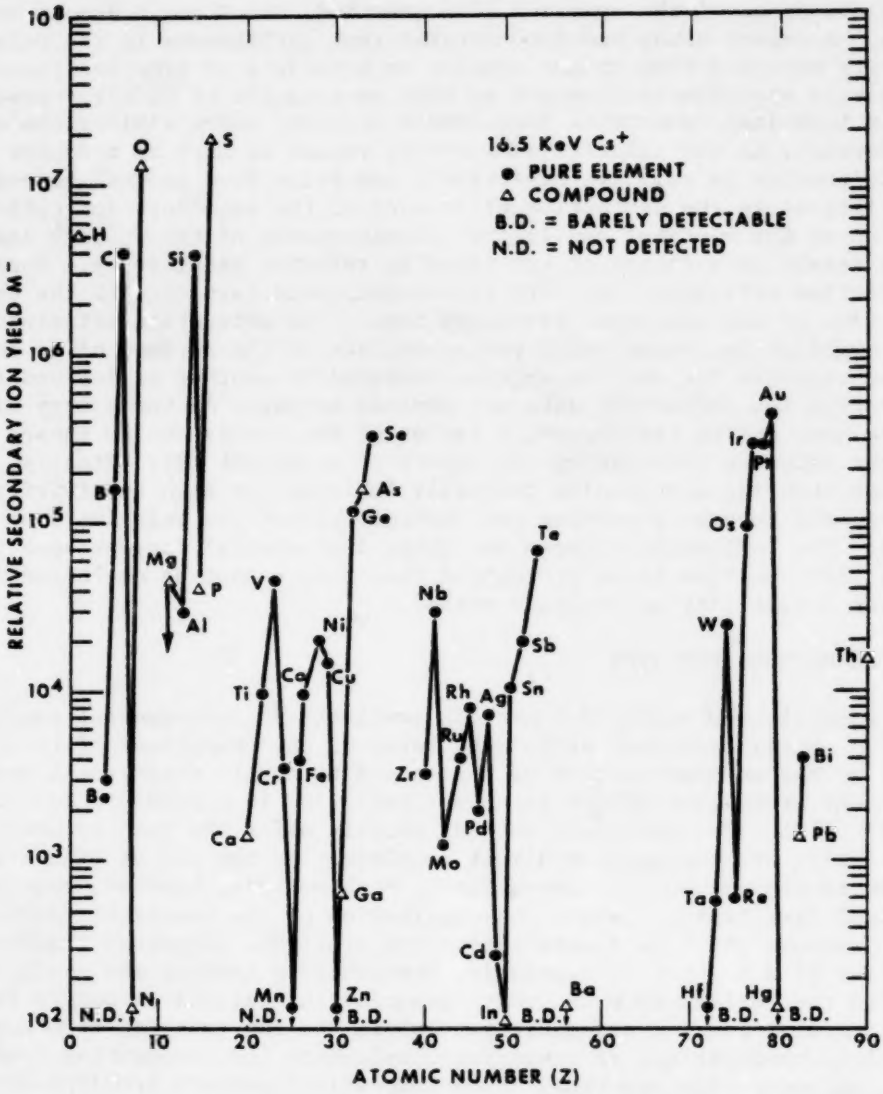

Figure 4. (b) Normalized negative secondary ion yields under Cs^+ bombardment (5).

existence of instrumental variations in the relative sensitivity. The relative sensitivity, $S_{X/M}$, is defined as:

$$S_{X/M} = (i_X/C_X f_X)/(i_M/C_M f_M) \quad (1)$$

where i is the secondary ion signal, C is the atomic concentration, f is the isotopic abundance of the spectral line measured, and X and M denote any two elements. A recent study has demonstrated that differences in the relative sensitivity measured from common samples on a variety of SIMS instruments with magnetic spectrometers ranged as high as a factor of 50 (7). Even on nominally identical commercial instruments operated under similar conditions, the differences in the relative sensitivity ranged as high as a factor of 10. These differences in relative sensitivity can arise from several sources (8, 9). Variations in the extraction efficiency of the secondary ion optics as a function of the vertical and lateral displacements of the primary ion optic axis can result in a factor of two range in relative sensitivity. Moreover, the extraction efficiency can vary in a complicated fashion with the energy distribution of the sputtered secondary ions. The extraction efficiency can also be modified by charge which can accumulate at the surface of an insulator. The response for one ion species compared to another as derived from the Daly-type ion conversion detector depends strongly on the energy with which the ions strike the target; a factor of two change in ion energy can affect the relative response by two orders of magnitude (9). Finally, in the single-ion counting electronics typically employed for high sensitivity detection, the threshold setting can markedly affect the relative ion response. The influence of these and other instrumental factors upon the measured SIMS spectrum is so pronounced that they cannot be neglected in developing a quantitative analysis method.

ANALYTICAL METHODS FOR SIMS

In general, the analytical methods available in instrumental analysis range from purely empirical techniques based on the comparison of the spectrum measured on the unknown to that of a standard to purely theoretical methods in which the production of the secondary radiation is completely described physically (10). The empirical methods usually offer the best accuracy, since matrix effects are compensated almost completely by the use of standards which are close to the unknown in composition. Such methods, however, have poor "analytical flexibility", since the application of the empirical techniques to a new unknown which is dissimilar to the available standards requires the fabrication of a new set of standards, frequently a tedious and costly process. The theoretical methods, which describe the emitted secondary from physical models, can, in principle, calculate the ion emission from any hypothetical composition, or conversely, calculate the composition from any measured secondary ion spectrum. Such theoretical methods are dependent on the availability of many material constants, including work functions, partition functions, etc., so that even if a model accurately describes the process of secondary ion emission, the compositional accuracy which is achieved may be poor due to uncertainty in the reference data.

Empirical Methods

Absolute Sensitivity Factors--

An absolute sensitivity factor, S_X, can be defined as:

$$S_X = i_X/C_X \qquad (2)$$

where i is the intensity measured for an element X in a standard of known composition C. Analysis of an unknown with absolute sensitivity factors requires a set of standards containing all elements of interest and a defined set of operating conditions, since the measured intensity is a function of the primary ion species, the beam current and energy, the secondary ion extraction efficiency, and the detector gain. The absolute sensitivity factor method contains no inherent correction for matrix effects. This method can only be applied to SIMS analysis when standards are available which are close in composition to the unknown. By measuring the absolute sensitivity factors on the same instrument used for the analysis of the unknowns and operating under defined conditions, instrumental discrimination effects can be almost completely eliminated.

Working Curves--

A "working curve" establishes the instrumental signal response as a function of concentration in a given matrix from a series of standards. Examples of SIMS working curves are shown in Figures 5 (a) and (b). A working curve is an elaboration of the absolute sensitivity factor method. A suite of standards is employed which spans the composition range of interest for the unknowns. Analysis of the unknown is carried out directly by comparing the signal measured on the unknown with the working curve to yield the predicted concentration. SIMS working curves are usually simple linear functions for those samples in which the solute element is present at low concentrations (e.g., 10 atom percent or less) and situated in only one phase. Non-linearities in the working curves are frequently observed at high concentrations or in cases in which an element is partitioned in two or more phases. Analytical accuracies of five percent relative can be achieved with the working curve approach, even in the case of non-linear response, provided sufficient standards are available to define the working curve. Working curves inherently incorporate instrumental discrimination effects, and hence must be locally determined. No matrix corrections are contained in the working curve function, so the method does not have flexibility in the analysis of unknowns.

Relative Sensitivity Factors--

The relative sensitivity factor, $S_{X/M}$, defined by equation (1), can also be employed for quantitative analysis. By algebraic manipulation of equation (1), the measured ratio of secondary ion intensities for two elements X and M can be related to the ratio of concentrations, providing the appropriate relative sensitivity factor is available from measurements on known standards:

$$C_X/C_M = (I_X/I_M)(1/S_{X/M}) \qquad (3)$$

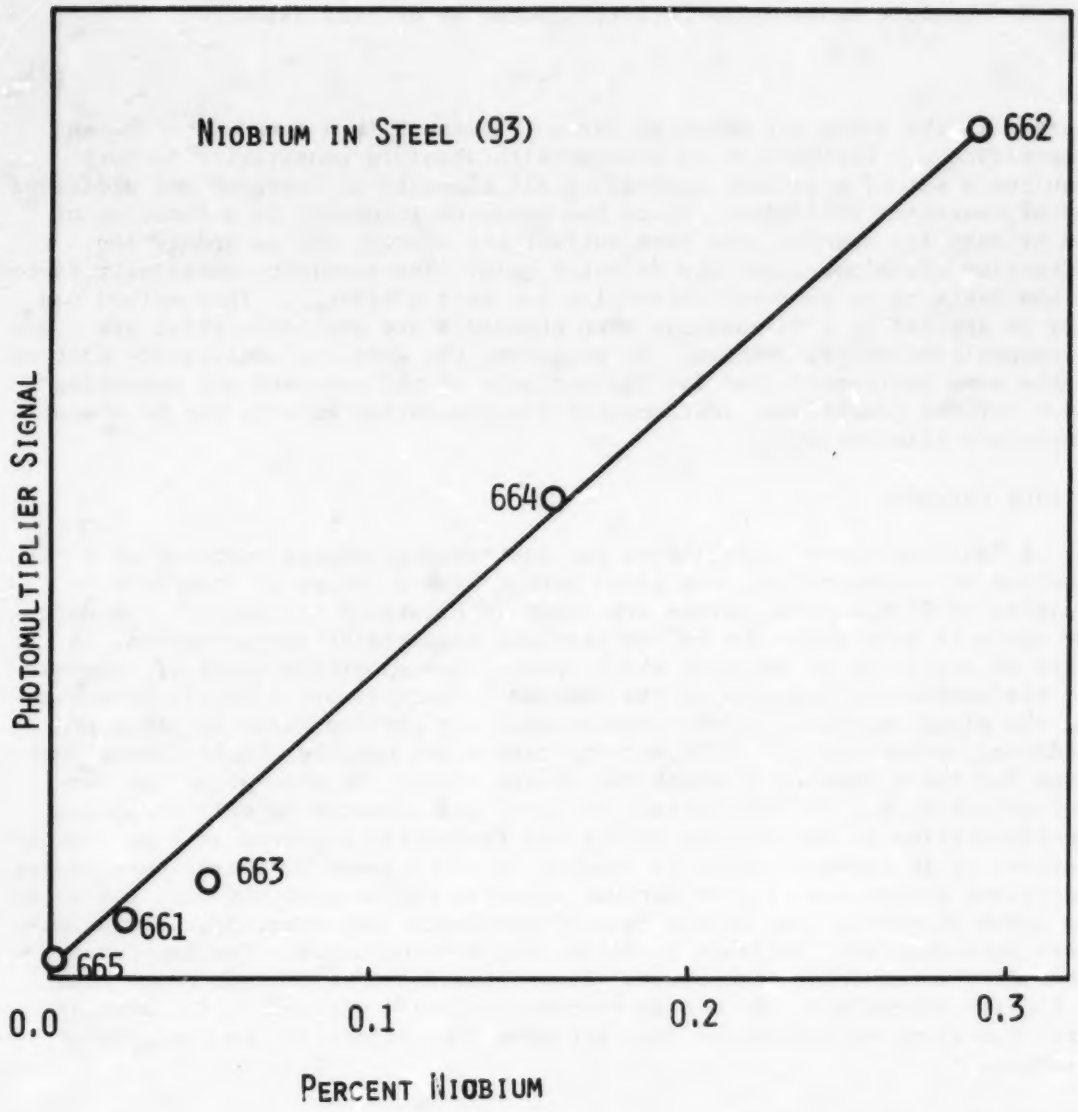

Figure 5. (a) Working curve for niobium in an iron matrix (NBS SRM 660 steels).

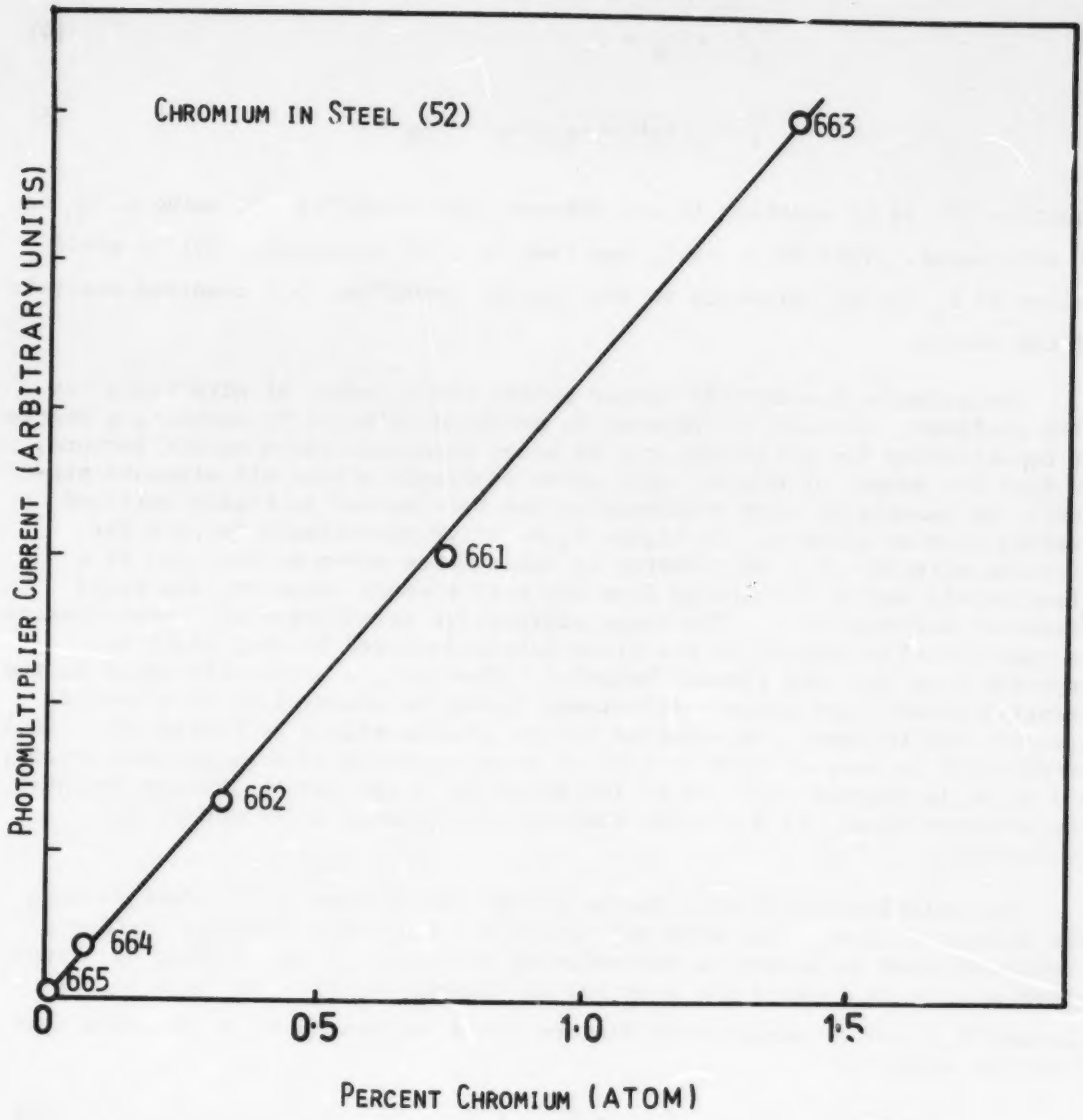

Figure 5. (b) Working curve for chromium in an iron matrix.

where I = i/f is the total secondary ion signal for an element considering all isotopes. By measuring (I_X/I_M) for all elements in a sample,

$$\sum_i C_X + C_M = 1 \tag{4}$$

$$\sum_i (I_X/I_M)(1/S_{X/M})C_M + C_M = 1 \tag{5}$$

Equation (5) is an equality in one unknown, and therefore the value of C_M can be determined. This value of C_M can then be used in equation (3) to yield values of C_X for all elements in the sample, resulting in a complete analysis of the sample.

The relative sensitivity factor method has a number of advantages for SIMS analysis. Because one element is measured relative to another, a degree of compensation for matrix effects is often obtained, since matrix factors, such as the amount of oxygen, will often similarly affect all elements present. An example of this compensation can be observed in highly oxidized systems such as glasses. In Figure 6, relative sensitivity factors for elements with $20 \leq Z \leq 32$ compared to silicon are shown as measured in a glass matrix and as calculated from the pure element secondary ion yield values of Andersen (11). The range of relative sensitivity for these elements is substantially reduced in the glass matrix compared to what might be expected from the pure element behavior. Moreover, a systematic trend in the relative sensitivity factor with atomic number is observed in this period. Similar results have been reported for an alumina matrix by McHugh (2). In a matrix rich in oxygen, such as a glass which contains 60 atom percent oxygen, and which is further enriched by implantation of the oxygen primary ion beam, the elements behave in a similar fashion with respect to secondary ion production.

The relative sensitivity factor method has another useful feature when the analyst is confronted with an unknown which differs from the standards previously used to determine the suite of factors. If the analyst has determined a suite of factors for a series of elements X_i relative to a matrix element M, a set of sensitivity factors for a new matrix N can be calculated from the equation:

$$S_{X/N} = S_{X/M} \cdot S_{M/N} \tag{6}$$

An example of the application of this equation for generating new sensitivity factors is given in TABLE 1, where calculated and measured sensitivity factors are compared for a germanium--oxygen system derived from a silicon-- oxygen system. In this case, the errors introduced by calculating the sensitivity factors are generally less than a factor of two. This procedure works most satisfactorily for highly oxygenated systems such as glasses, ceramics, minerals, etc., in which a reactive species provides a common matrix element.

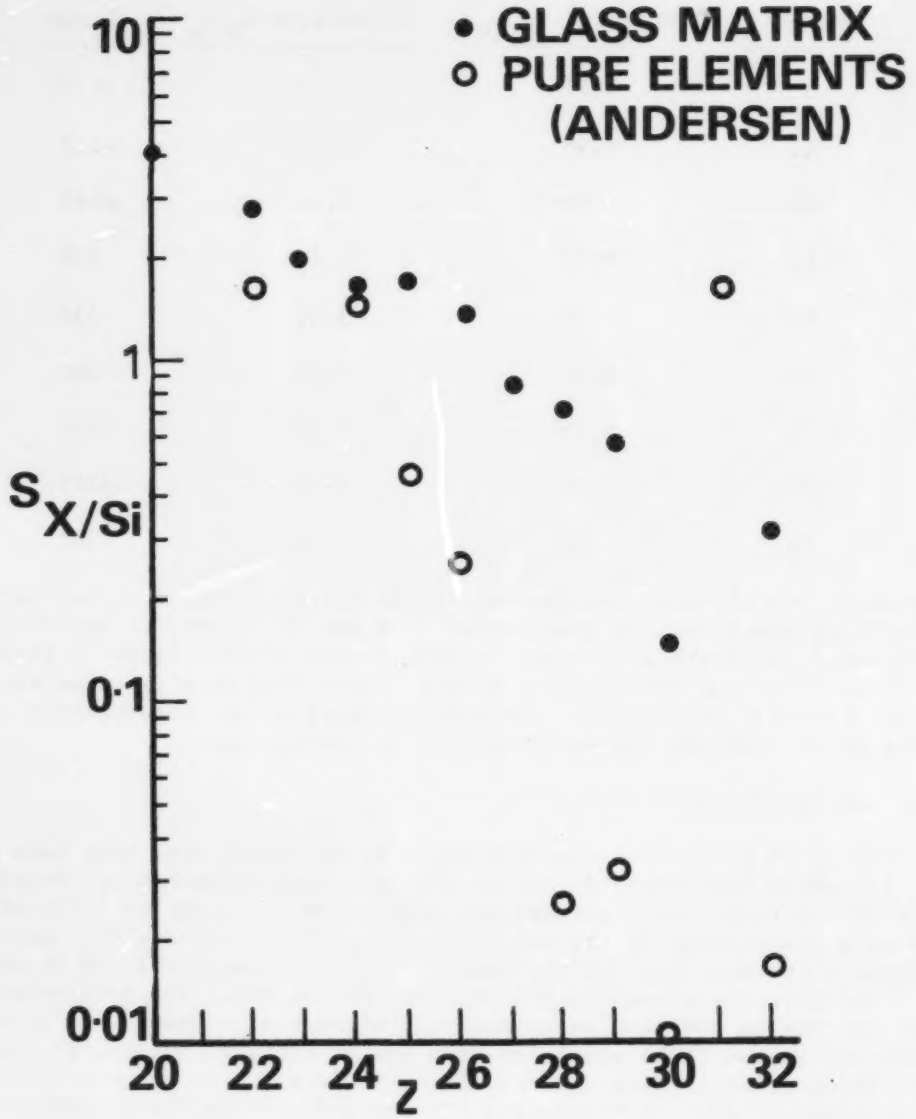

Figure 6. Relative sensitivity factors for selected elements compared to silicon as measured in a glass matrix and as calculated from pure element data (11).

TABLE 1. COMPARISON OF MEASURED AND CALCULATED RELATIVE SENSITIVITY FACTORS

Element	Measured $S_{X/Ge}$	Calculated $S_{X/Ge}$	Error
B	0.77	0.78	+1.3%
Al	9.98	7.51	-25%
Si	1.66	2.56	+54%
Ti	9.71	7.12	-27%
Fe	4.52	3.02	-33%
Zr	6.97	5.00	-28%
Ce	5.75	7.00	+30%
Ta	0.49	0.60	+22%
Pb	1.69	1.18	-30%

Relative sensitivity factors inherently contain local instrumental bias and therefore should not be transferred from one instrument to another. As such, however, analysis with relative sensitivity factors tends to eliminate errors resulting from instrumental effects, providing care is taken to establish the same standardized operating conditions for the analysis of the unknowns as is used for the determination of the factors.

Theoretical Models for SIMS Analysis--

A number of models for the production of secondary ions have been proposed, including thermodynamic models (12,13), quantum mechanical models (14), valence models (15), and electrostatic models (16,17). The validity of these models as a description of the secondary ion emission process is a matter of considerable debate. Most of the models have only been developed to the point of considering secondary ion emission during noble ion sputtering of elements or simple compound targets in the absence of oxygen. The local thermal equilibrium (LTE) model has been one of the most successful models in describing secondary ion spectra of multi-element systems under reactive ion bombardment (12). In brief, the LTE model describes the secondary ion emission as originating in a dense plasma at the surface of the target. The plasma is assumed to be in thermal equilibrium, allowing application of the Saha-Eggert equation to relate the sputtered ion/neutral ratio in the plasma to several parameters.

$$\log_e(n^+/n^o) = 15.4 + 1.5\log_e T + \log(2B^+/B^o) - \frac{5040}{T}(I_p - \Delta E) - \log_e n^- \qquad (7)$$

where n^+ and n^o are the numbers per unit volume of ions and neutrals for a given element, B is the partition function, I_p is the ionization potential, ΔE is the depression of the ionization potential, T is the plasma temperature, and n^- is the density of free electrons. With the exception of T and n^-, the other parameters in equation (7) can be obtained from reference data. In applying the LTE model to an unknown sample, the temperature and electron density are, in general, not known in advance. In some cases, these parameters can be obtained from previous experiments on similar samples of known composition. Alternatively, in the "internal standard" LTE method, the known compositions of two elements in the sample and the measured secondary ion intensities for those elements are used to solve equation (7) as a system of simultaneous equations in the variables T and n^-. The values of T and n^- thus determined are used to relate the measured secondary ion intensities n_i^+ for the remaining elements in the sample to the numbers of neutral atoms n_i^o in the sputtered assemblage, which yields the composition. In further elaborations of the LTE model, negative secondary ions, molecular ions, and multiply-charged ions can be considered (12).

It is important to note that the LTE model, as well as the other theoretical models, calculate the ion-to-neutral ratio as emitted from the sample. The ion signal actually measured differs significantly from the emitted ion signal, since the spectrometer transmission is only of the order of 0.1 - 10 percent. If the transmitted signals were proportional to the emitted signals with the same constant of proportionality for the ions of all elements, the loss due to transmission could easily be compensated. However, the transmission is usually mass dependent, and the ion detection system can also give a mass dependent response, and the ion detection system can also give a mass dependent response, so that the overall system response is a complicated function of mass. Analysis with a theoretical model which does not incorporate any corrections for the instrumental response can be in error by as much as an order of magnitude. Often, these errors in analysis are taken to be evidence of the failure of a model to describe secondary ion emission when, in fact, the errors are associated with the measurement process.

COMPARISON OF RESULTS OF QUANTITATIVE ANALYSIS METHODS

To compare the accuracy which could be achieved with the relative sensitivity factor method and with the LTE theoretical matrix correction method, Newbury and Heinrich studied a system of multi-element glasses as a model system (18). Glasses offer a number of advantages as model system for SIMS analysis: (1) Glasses can be prepared with many combinations of elements in a single matrix which is homogeneous at the micrometer scale of spatial resolution. (2) The oxygen content of glasses is typically 60 atom percent, which is further increased by implantation of the primary oxygen ion beam. Secondary ion emission from such an oxygen-rich system is less susceptible to artifacts introduced by gases adsorbed from the specimen vacuum environment. (3) A common element, such as silicon, can be included in the compositions of the various glasses to provide a reference element for the relative sensitivity factors.

For assessing the accuracy of analysis, an error factor, F, was defined as,

$$F = C(\text{true})/C(\text{calculated}) \qquad (8)$$

where C is the atomic concentration.

Analysis of Glasses by Relative Sensitivity Factors

In the analysis of the glasses by the relative sensitivity factor method, average values of the relative sensitivity factors were first determined from a group of glasses, and these average values were then employed for the analysis of a large suite of glasses. The resulting histogram of error factors for more than 100 elemental determinations is shown in Figure 7. The error distribution is such that 83 percent of the analyses fall within an error factor of two, and 99 percent fall within an error factor of five. No error factors greater than seven were observed. Closer examination of the error distribution near unity reveals that 53 percent of the analyses fall within an error factor of 1.2.

This study was extended to simulate the analysis of unknowns by conducting a "blind sample round robin" (19). In this study, four laboratories which had previously been supplied with a suite of glasses for the determination of relative sensitivity factors were asked to analyze an additional group of glasses as unknowns. In this case, each laboratory selected relative sensitivity factors from the reference standards which most closely matched the unknowns. The analytical performance for this situation is summarized in the error histogram of Figure 8. The error distribution is such that 91 percent of the analyses fall within an error factor of two, and 100 percent within a factor of five.

LTE Analysis of Glasses

Analysis of the suite of glasses was also carried out with the LTE model in the method devised by Andersen and Hinthorne (12). Two elements were selected as the internal standards, and the true composition values for these elements were used as input to the calculation. The sum of the elemental composition other than oxygen was constrained to a total of 40 atom percent. Analyses were made with and without corrections for the molecular ions in the spectrum. No corrections were included for instrumental discrimination. The resulting error factor distribution, Figure 9, reveals that 53 percent of the analyses fell within a factor of two, and 84 percent within a factor of five. Error factors greater than five were observed in 16 percent of the analyses, with error factors in excess of 10 in about 5 percent of the cases. Error factors as high as 40 were observed for heavy elements such as lead and tantalum.

Comparison

When the error factor distributions in Figures 7, 8, and 9 are compared, the relative sensitivity factor method is clearly seen to produce superior overall results. In particular, analysis with the relative sensitivity factor

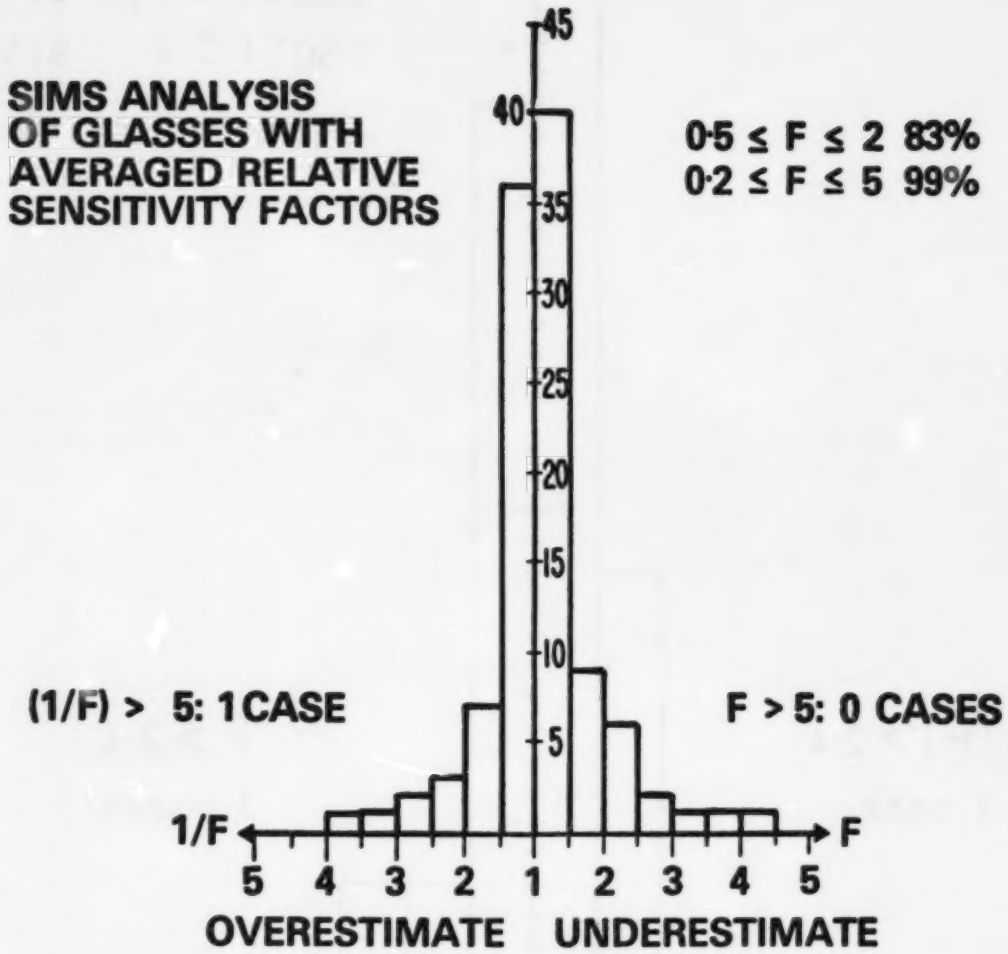

Figure 7. Error factor histogram for quantitative analysis of glasses by the relative sensitivity factor method with average values of sensitivity factors (4).

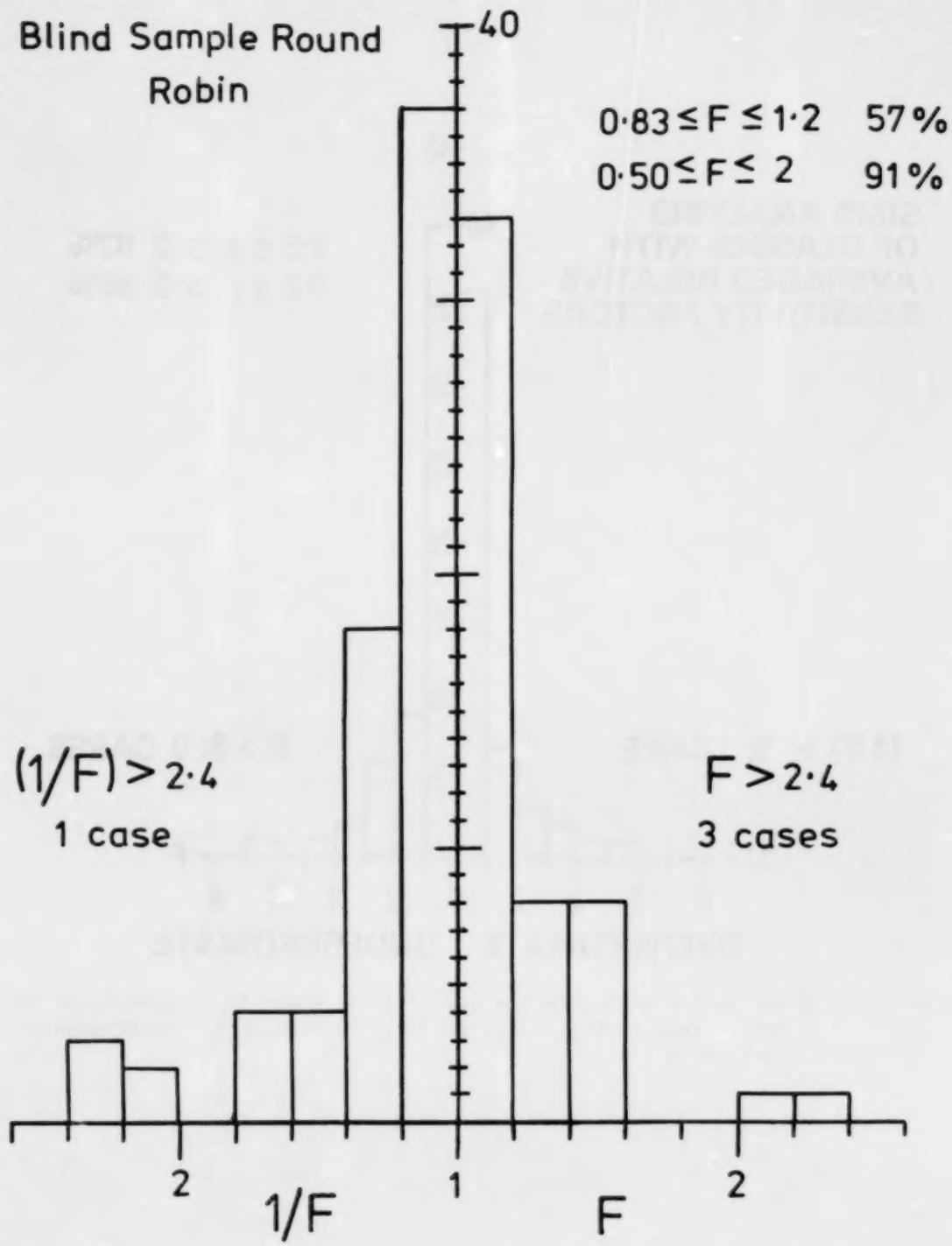

Figure 8. Error factor histogram for quantitative analysis by the relative sensitivity factor method. Blind round robin results on unknown glasses (19).

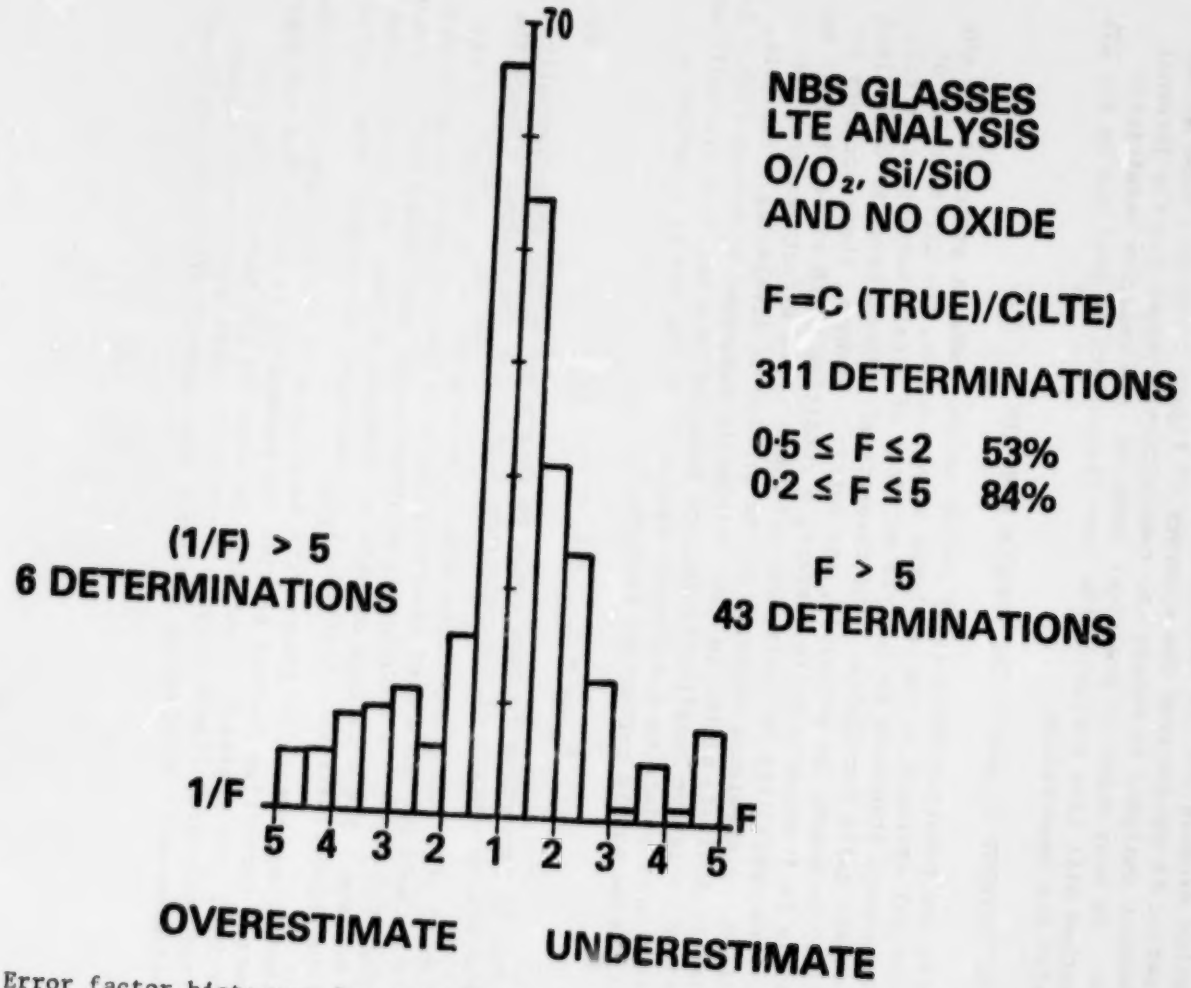

Figure 9. Error factor histogram for quantitative analysis of glasses by the local thermal equilibrium model method (4).

method greatly reduces the number of large errors exceeding a factor of five. While the amount of standards data required for the relative sensitivity factor method exceeds the LTE method, it must be noted that application of the LTE method to obtain even the accuracy of Figure 9 requires some method of independent analysis to obtain the compositional values for the internal standards. In many cases of practical interest, the relative sensitivity factor method will give virtually the same flexibility in analysis as the LTE method with its constraints.

FUTURE DEVELOPMENT OF ANALYTICAL METHODS FOR SIMS

While the relative sensitivity factor method seems at present to be the most practical approach to the analysis of an unknown, the difficulties of obtaining enough standards to analyze matrices of widely varying electronic character are quite formidable. The theoretical methods have the analytical flexibility to solve, in principle, any matrix. However, their accuracy in an analysis is frequently quite suspect, a condition which arises in part due to their susceptibility to instrument artifacts which affect measured ion intensities. A promising approach to the problem of developing a flexible, quantitative analysis method is that originally suggested by McHugh (20). In this method, relative sensitivity factors measured in a matrix M are modified to factors appropriate to a different matrix M' by the use of a series of multiplicative matrix correction factors, S_i:

$$S_{X/M'} = S_{X/M} \cdot \Sigma_1 \cdot \Sigma_2 \cdot \Sigma_3 \ldots \quad (9)$$

These matrix correction factors could be determined either experimentally from the actual spectra of the reference sample and the unknown through the measurement of a matrix sensitive signal, such as M^{++}/M^{+} or MO^{+}/M^{+}, or the Σ factors could be calculated theoretically with the LTE model or an alternative physical model. A combination of experimental and theoretical Σ factors could be used. The advantage of such an approach is that the locally determined relative sensitivity factors, $S_{X/M}$, measured for example from a suite of glasses, automatically incorporate local bias in the instrumental response. The matrix correction factors provide the capability to shift from one matrix to another. The approach illustrated in equation (9) should offer the required analytical flexibility to successfully deal with a wide variety of specimens while eliminating the large instrumental effects on analysis.

4. EXPERIMENTAL METHODS

SPECIMEN CHARGING

Most particles of interest derived from environmental sources are found in the form of chemical compounds, such as oxides or sulfides, rather than as pure elements. This is an important distinction, since compounds tend to be electrically insulating, while many pure elements have a conducting or semiconducting nature. Under charged ion (or electron) beam bombardment, insulating particles tend to accumulate electrical charge. When a sufficient charge is developed, the particles often repel each other, causing a change in position of the target of interest. In extreme cases, the particles may be ejected from the substrate and lost.

In SIMS, the analyst has a choice of either a positive primary ion beam (usually $^{16}O_2^+$, $^{14}N_2^+$, $^{40}Ar^+$, or $^{133}Cs^+$) or a negative primary ion beam ($^{16}O^-$, or N_2O^-). The source brightness (in A/cm^2) is typically 10 to 100 times brighter for a positive primary ion compared to a negative primary ion (e.g., $^{16}O_2^+$ compared to $^{16}O^-$). Thus, in terms of the beam current obtained in the final probe, which is one of the determining factors in establishing the limit of sensitivity, it is more desirable to employ a positive primary ion beam. However, bombardment with positive primary ions tends to lead to significant problems with specimen charging.

Under the impact of a primary ion, regardless of its charge, secondary electrons are emitted from the target. The secondary electron emission coefficient under ion bombardment is frequently greater than unity. When a positive primary ion beam such as $^{16}O_2^+$ strikes the particle injecting positive charges, and secondary electrons are emitted, removing negative charges, the particle tends to acquire a positive charge. This positive charge can cause the positional instability mentioned above and can also affect the trajectories of the sputtered secondary ions, causing unstable signals or reducing the sensitivity. With negative primary ion bombardment, negative charges are injected into the target, while the emission of secondary electrons effectively removes negative charges. As a result of this flow of negative charge both to and from the target, a charge balance can be obtained. While the surface potential may not be at earth, a potential of the order of a few volts is not exceeded, and moreover, the potential is stable. Strong, stable secondary ion signals can be obtained. Thus, bulk insulating samples, such as oxidic materials, can be studied, see for example Figure 10. Secondary ion spectra from bulk insulators could not be obtained under positive

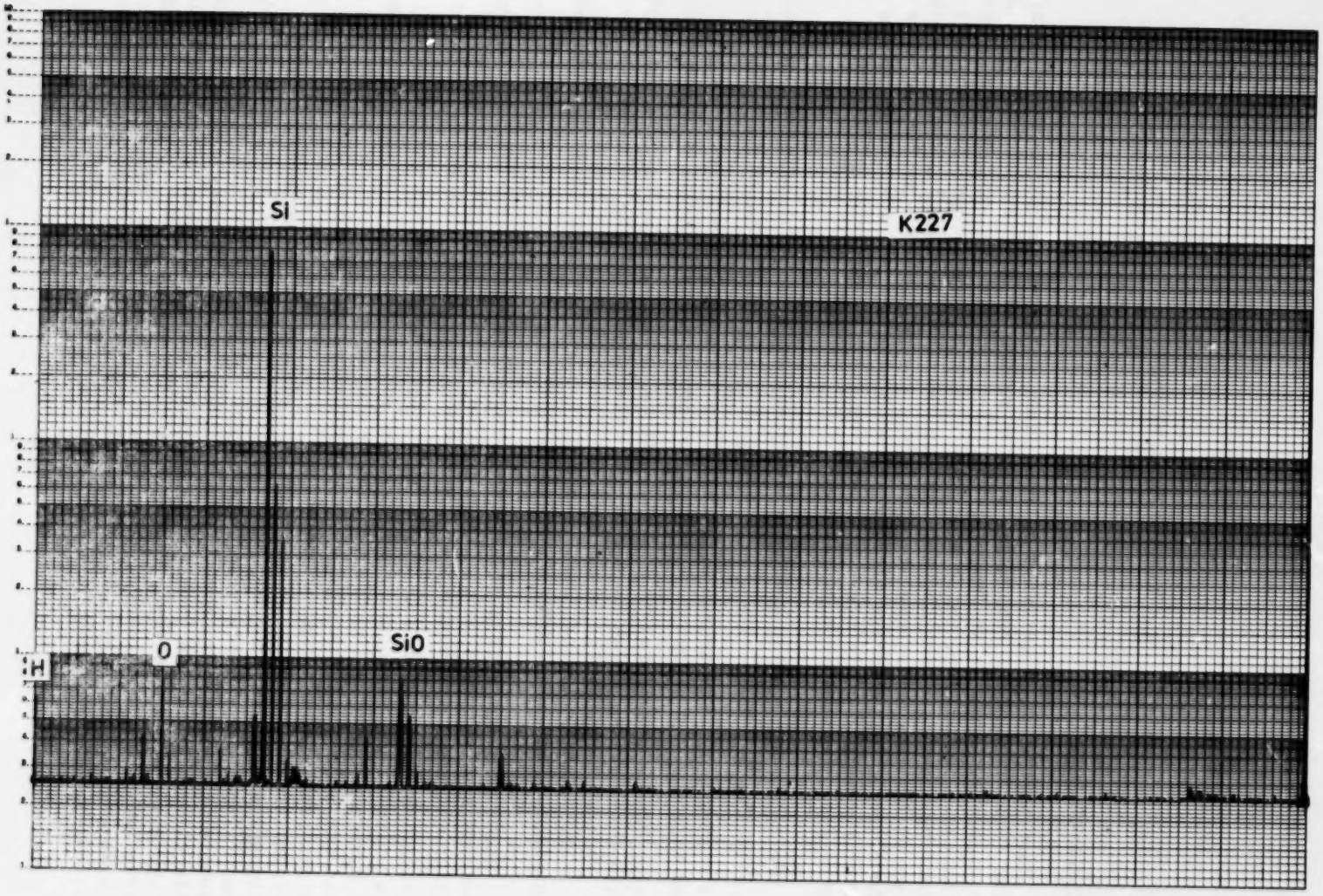

Figure 10. Spectrum of bulk NBS glass K 227 obtained with negative primary ions.

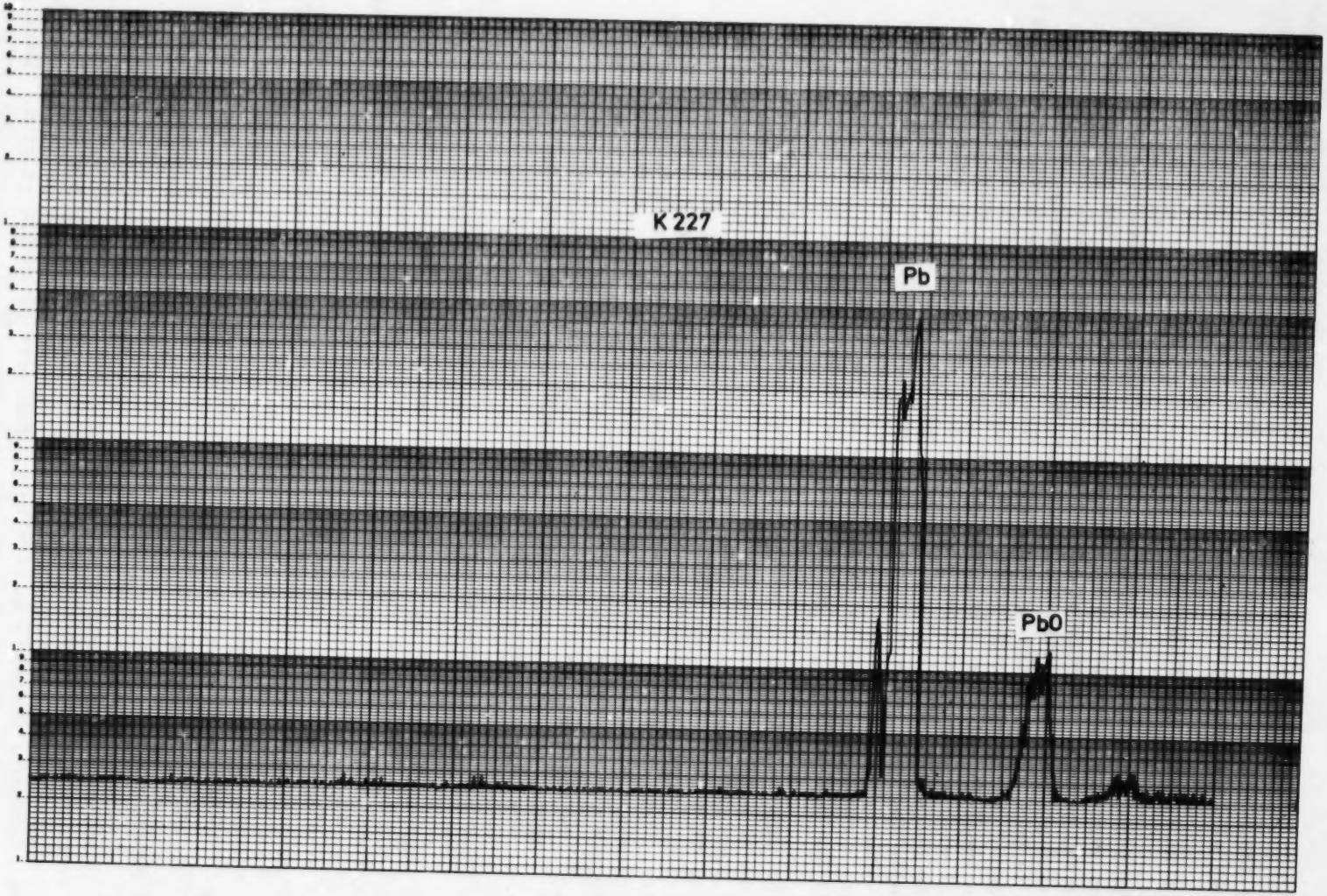

Figure 10 continued. Spectrum of bulk NBS glass K 227 obtained with negative primary ions.

primary ion bombardment. Negative primary ions were initially employed for the study of individual particles.

PARTICLE DISPERSION AND MOUNTING

The ideal substrate for SIMS study of individual particles is one which produces very few secondary ions. When positive secondary ion spectra are considered, several elements stand out as candidate materials. Of these, carbon and gold are most feasible. A second desirable property of the substrate is high reflectivity to aid in location of the particle via the optical microscope. While vitreous carbon can partially satisfy this requirement, gold is ideal in all ways. In addition, by choosing a high atomic number material with a single isotope, the possibility of introducing extraneous peaks in the spectrum is reduced. Gold substrates were prepared either from electroplating onto polished brass blocks or by pressing gold wire into thin foils. Particles were dispersed onto these substrates by ultrasonification in ethyl alcohol, followed by rapid drying on the substrates. For negative primary ion bombardment, no further preparation was needed.

The substrate typically contributed only sodium and gold signals to the spectrum of a particle. When measuring a spectrum on a particle, the gold signal from the substrate was found to be higher than when the substrate was measured directly. This was attributed to the resputtering of components of the particle from the adjacent substrate surface. For example, the silicon sputtered from the particle contaminated the surface of the gold, increasing the ionization efficiency of the gold compared to the clean substrate. In addition to the elemental gold secondary ion signal, a molecular signal for $^{213}(AuO^{+})$ is observed which is frequently higher than the parent $^{197}Au^{+}$ signal. Again, this is attributed to the presence of sputtered material on the substrate near the particle under analysis.

USE OF POSITIVE PRIMARY ION BEAMS

In order to maximize sensitivity from small particles, experiments were carried out to explore the possibility of employing high brightness positive primary ion beams. Particles were dispersed onto gold substrates as described above. Coatings of thermally-evaporated high purity carbon of various thicknesses were applied. With carbon coatings of the order of 20 - 40 nm thick, stable secondary ion signals could be obtained from individual particles less than 10 μm in diameter, Figure 11. Since positive ion beams with a diameter of 1 μm could be generated, the use of positive ions allows the study of inhomogeneities in heterogeneous particles with sub-structure on the order of the beam size.

DEPTH PROFILING

In order to study layered particles, the depth profiling mode of operation of the ion microprobe has been employed extensively. Since the sample is continuously sputtered in order to generate the secondary ion signal, control of the sputtering process can lead to a known rate of sample erosion. Thus, the sample can be effectively "peeled" atom layer by atom layer. By monitoring the secondary ion signals as a function of erosion time, elemental depth

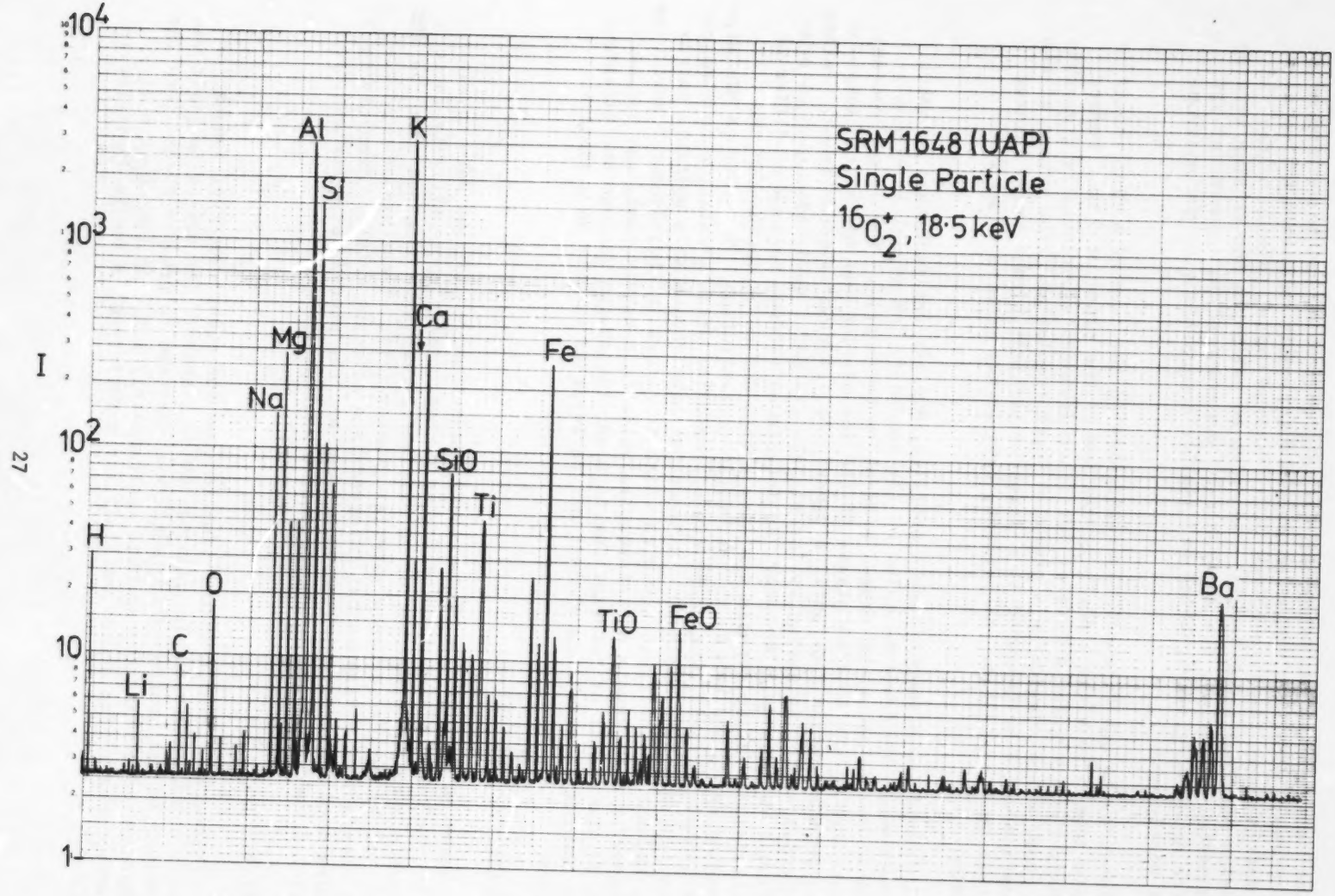

Figure 11. Spectrum of a single particle obtained with a positive primary ion.

profiles can be obtained, providing the rate of erosion can be determined. In the present work, the particles examined typically contained silica as a major matrix constituent, combined with aluminum oxide, calcium oxide, and iron oxide at significant levels. In order to calibrate the erosion rate on environmental particles, the erosion rate was measured on a number of NBS Research Material glasses, which had similar compositions to the environmental particles.

Ion erosion can be carefully controlled in the case of a flat, semi-infinite sample to yield a depth resolution of the order of 5 nm. Unfortunately, the irregular nature of particles deviates substantially from this ideal case, which results in a degraded depth resolution. The extent of the degradation could be measured if a suitable particle with a known layered structure were available. At present, this factor remains to be fully evaluated.

In preparing elemental depth profiles, another artifact must be taken into account. The absolute value of the secondary ion signal is strongly dependent on the amount of oxygen present in the matrix. The oxygen content can vary during the initial stages of the ion erosion due to the implantation of the primary oxygen ions until a dynamic equilibrium is established. During this period, absolute secondary ion signals are not a good indication of compositional variations. Moreover, at interfaces between regions of different composition, absolute signals can also change due to variations in the sputtering rate, and hence, in the oxygen concentration. In order to minimize these dynamic effects, the technique of measuring signals relative to a major matrix peak has been employed. Silicon has been chosen as a suitable matrix peak, because of the frequency with which it occurs in environmental particles. By measuring the signals of interest relative to a matrix peak, the variations in the signal of interest due to a varying oxygen content are minimized since the matrix reference element can be expected to vary in a similar fashion.

QUANTITATIVE ANALYSES

Based on the results of Section 2, quantitative analyses were carried out by the relative sensitivity factor method. Relative sensitivity factors appropriate to the situation of an oxidized matrix were obtained from the NBS RM 30 and 31 series research material glasses (21). These glasses contain most elements of environmental interest in a silicate matrix. Sensitivity factors were measured relative to silicon and the procedures described in Section 2 were employed for quantitative analyses.

SENSITIVITY LIMITS

Sensitivity limits were estimated from the count rates per nanoamp of primary ion beam current on selected RM 30 glasses. The detection limit was estimated as the concentration which was expected to produce three times the background count rate (background approximately 1 c/s in the absence of interferences). The detection limit for a variety of elements is listed in TABLE 2.

TABLE 2. DETECTION LIMITS IN SILICON-LEAD-OXYGEN GLASS

(NBS K493 and K523 Glasses)

Element[a]	c/s/nA/Atom Percent[b]	1 nA detection limit[c] (1 sec. integration) ppm
Li	7.22×10^4	0.42
B	4.69×10^3	6.4
Mg	4.66×10^4	0.64
Al	6.32×10^4	0.47
P	1.32×10^3	23
Ti	5.37×10^4	0.56
Cr	3.01×10^4	1
Fe	1.77×10^4	1.7
Ni	1.13×10^4	2.7
Ge	7.45×10^3	4
Zr	4.20×10^4	0.71
Ba	7.41×10^4	4.0
Ce	1.85×10^4	1.6
Eu	6.45×10^4	4.6
Ta	2.51×10^3	12
Th	1.38×10^4	2.2
U	1.42×10^4	2.1

[a] All elements as dilute solutes in the indicated matrix.

[b] Corrected for mass abundance.

[c] Concentration which is expected to produce three times the background count rate (1 c/s).

5. DETECTION OF MOLECULAR SIGNALS BY SIMS

The secondary ion spectrum frequently contains ion species which do not correspond to elemental ions. Figure 12 shows a positive secondary ion spectrum of silicon bombarded with oxygen primary ions. The Si^+ elemental peaks are observed. In addition, a cascade of molecular peaks are observed, including SiO^+, Si_2^+, Si_2O^+, SiO_2^+, $Si_2O_2^+$, etc. In general, an oxidized structure containing metallic ions M^+ and N^+ can produce a wide variety of molecular ion signals, including $M_xO_y^\pm$, $N_xO_y^\pm$, $M_xN_x^\pm$, and $M_xN_yO_2^\pm$. These signals can be used to identify the presence of compounds within the original sample. However, the act of sputtering the sample can cause the breaking of chemical bonds and the creation of new molecular species within the ion-bombarded region. To properly interpret the inorganic molecular spectrum, it is necessary to study model systems in order to identify the characteristic molecular ions. In a complicated, multi-component environmental particulate, the multiplicity of possible molecular fragment ions can make spectral interpretation difficult. Only the molecular signals associated with the major constituents can be studied usefully.

Considerable interest has arisen in the past several years in the detection of organic compounds by means of SIMS (22,23). Benninghoven and his co-workers have successfully obtained SIMS spectra from a large number of organic compounds with parent ions in the mass range 50 - 300 AMU. Benninghoven determined that to optimize the detection of organic molecules, which might be decomposed by the action of the bombarding ions, it would be necessary to employ conditions of "static SIMS". In static SIMS, the damage cross section for the incident ion is minimized by employing a low primary ion beam energy, typically 1 - 5 keV, and also by using an extremely low primary ion current density, of the order of 1×10^{-9} A/cm^2. In order to produce a detectable signal, a primary beam current of 1 nA must be used, but the beam is defocused to approximately 1 cm in diameter. The total dose during the recording of a secondary ion mass spectrum (e.g., for 1000 s) is of the order of 10^{12} ions/cm^2 or less. The probability of a given lattice location being struck more than once by an incident ion is therefore very low, and the measured secondary ions are generated from undamaged material throughout the period of the experiment. While organic mass spectrometry by static SIMS is very promising, the study of particles by static SIMS is not feasible. Because of the low current density, useful signals could not be obtained from individual microscopic particles. Large aggregates of particles could be studied by static SIMS, but the results would only be valid if the sample was homogeneous on a particle by particle basis.

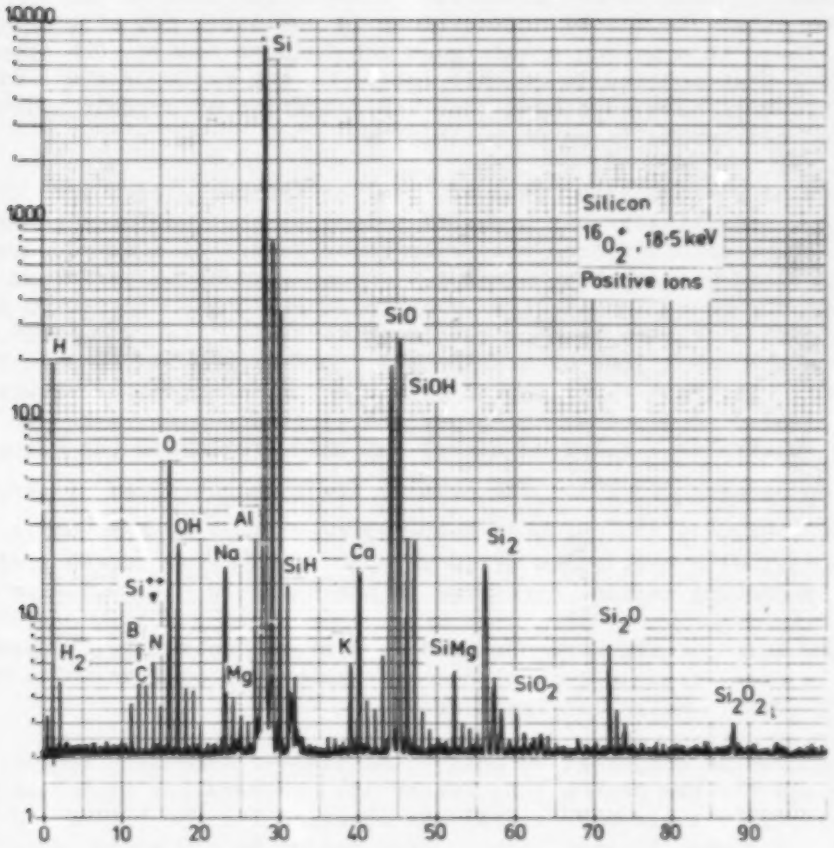

Figure 12. Secondary ion spectrum of pure silicon showing inorganic molecular signals.

The primary ion bombardment conditions which are employed in the ion microprobe deviate greatly from the condition of static SIMS and are considered to constitute "dynamic SIMS". In dynamic SIMS, the sample is effectively undergoing constant change during the measurement of a spectrum. The combination of a high bombardment energy (10 - 20 keV), which results in a large damage cross section, and a high current density (typically 1×10^{-1} to 1×10^{-3} A/cm^2), leads to the situation in which the dose is so high that all surface atom sites are hit by primary ions in the first few seconds of bombardment. Thus, if a molecule undergoes ion-induced damage, the opportunity for measuring that species is quickly lost. On the basis of these arguments, most investigators have concluded that the detection of organic molecules with the ion microprobe is an impossibility.

The ion microprobe does, however, have an extremely high specific sensitivity (i.e., sensitivity/unit bombarding ion) so that useful signals (100 - 1000 c/s) can be obtained from the major constituents of a sample even with a greatly reduced primary beam current. Investigations were carried out to determine if secondary ion spectra of organics could be obtained in a microprobe mode with a primary beam current density of 10^{-4} to 10^{-6} A/cm^2, which lies between the conditions of static SIMS (10^{-9} A/cm^2) and dynamic SIMS (10^{-1} A/cm^2). In these experiments, dilute water solutions of several organic compounds, including glycine, atropine, and fluorodopamine, were applied to metal film substrates, including nickel and gold, following the methods of Benninghoven et al., (22,23). The primary ion beam consisted of $^{16}O_2^+$ ions at 18.5 keV (effectively $^{16}O^+$ at 9.25 keV at interaction) or 8.5 keV (4.25 keV at interaction) with beam sizes of 10 µm - 50 µm and beam currents of 0.1 nA - 1 nA, producing current densities in the range 10^{-6} - 10^{-4} A/cm^2.

Complex mass spectra were obtained on a nickel substrate, Figures 13 and 14. Signals were obtained for molecular fragments as well as for nickel complexed with organic molecular fragments.

Fluorodopamine dispersed on gold films yielded secondary ion spectra with strong signals for the parent ion, Figure 15. In parallel with Benninghoven's observations (22), a stronger signal was observed for the parent molecule plus a hydrogen. A strong fragment peak corresponding to the parent minus an NH or CH_3 group was also observed. This experiment marks the first reported observation of the sputtering of intact large molecules under conditions which deviate substantially from the static SIMS case.

To evaluate the utility of this experiment for measuring organic layers on particles, a glycine solution was applied to spherical nickel particles with a diameter of approximately 20 µm. A portion of the mass spectrum obtained from a single nickel particle is shown in Figure 16. Note the similarity of this spectrum with the same portion of the spectrum obtained with glycine dispersed on a bulk nickel substrate. This experiment indicates the feasibility of obtaining useful organic mass spectra from layers on individual small particles, at least down to the size of 20 µm.

The ion microprobe employed in this experiment actually has a significant discrimination against molecular species due to the fact that its transmission

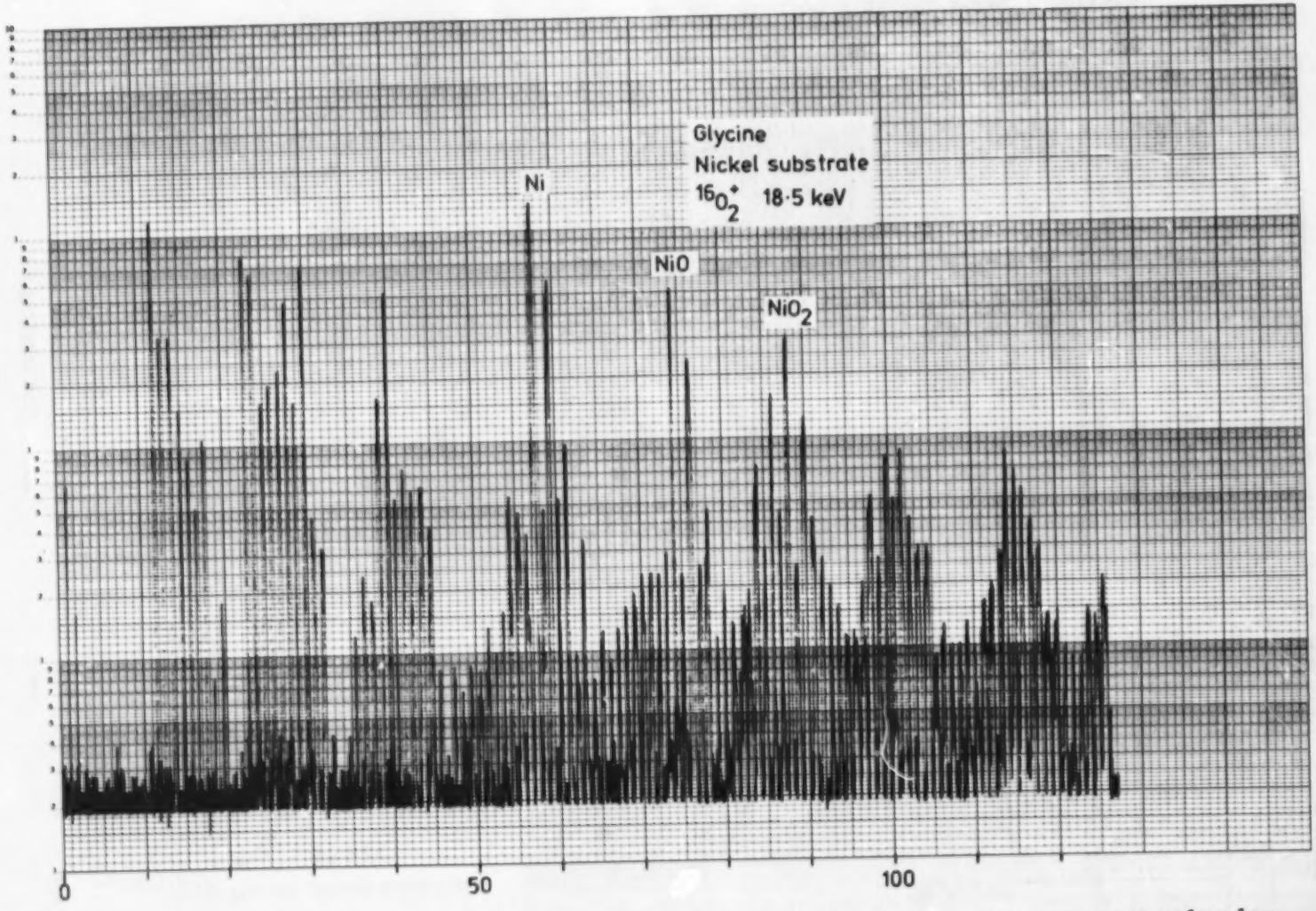

Figure 13. Secondary ion spectrum of glycine on a nickel sheet substrate showing numerous molecular fragments.

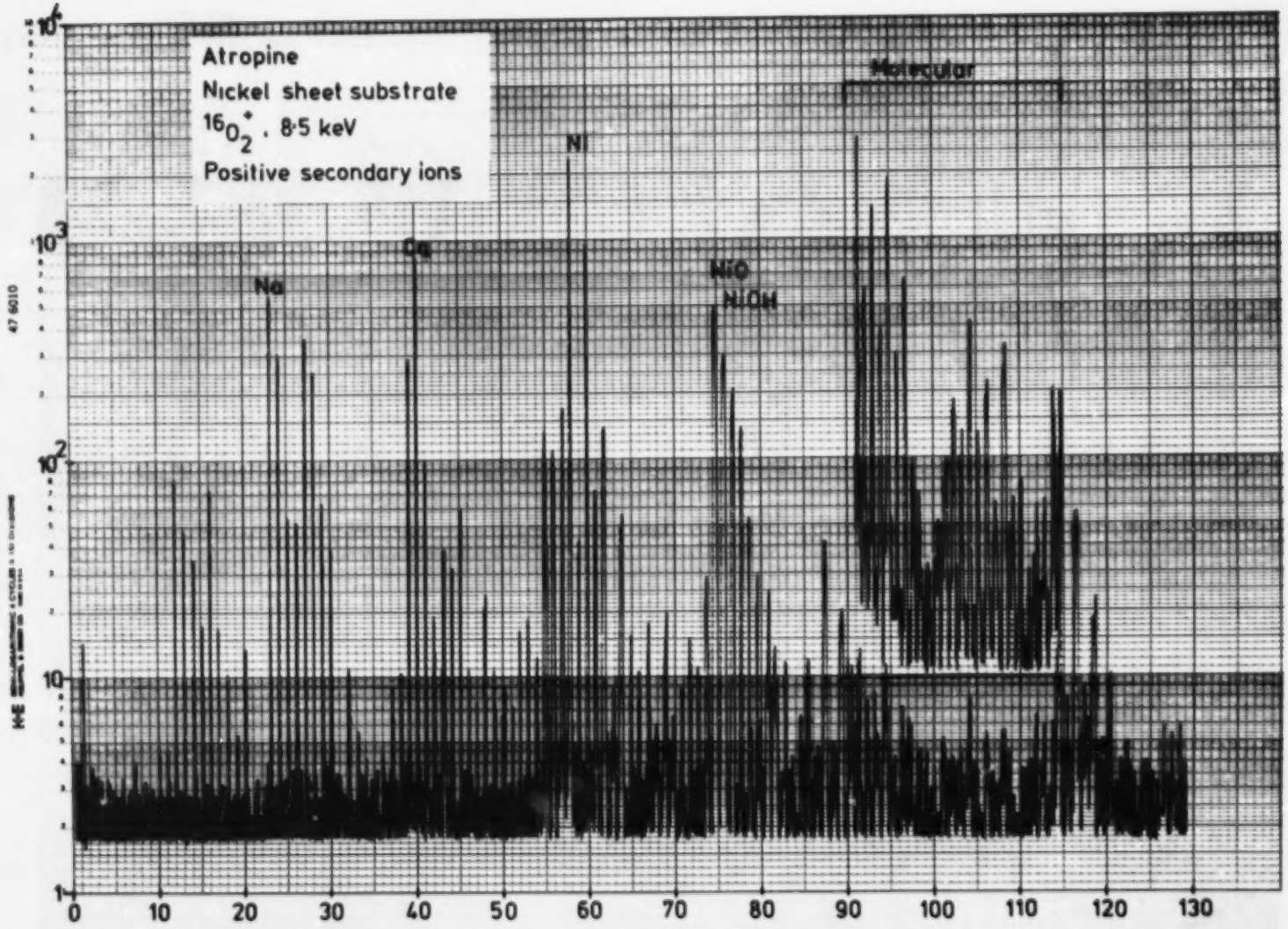

Figure 14. Secondary ion spectrum of atropine on a nickel sheet substrate.

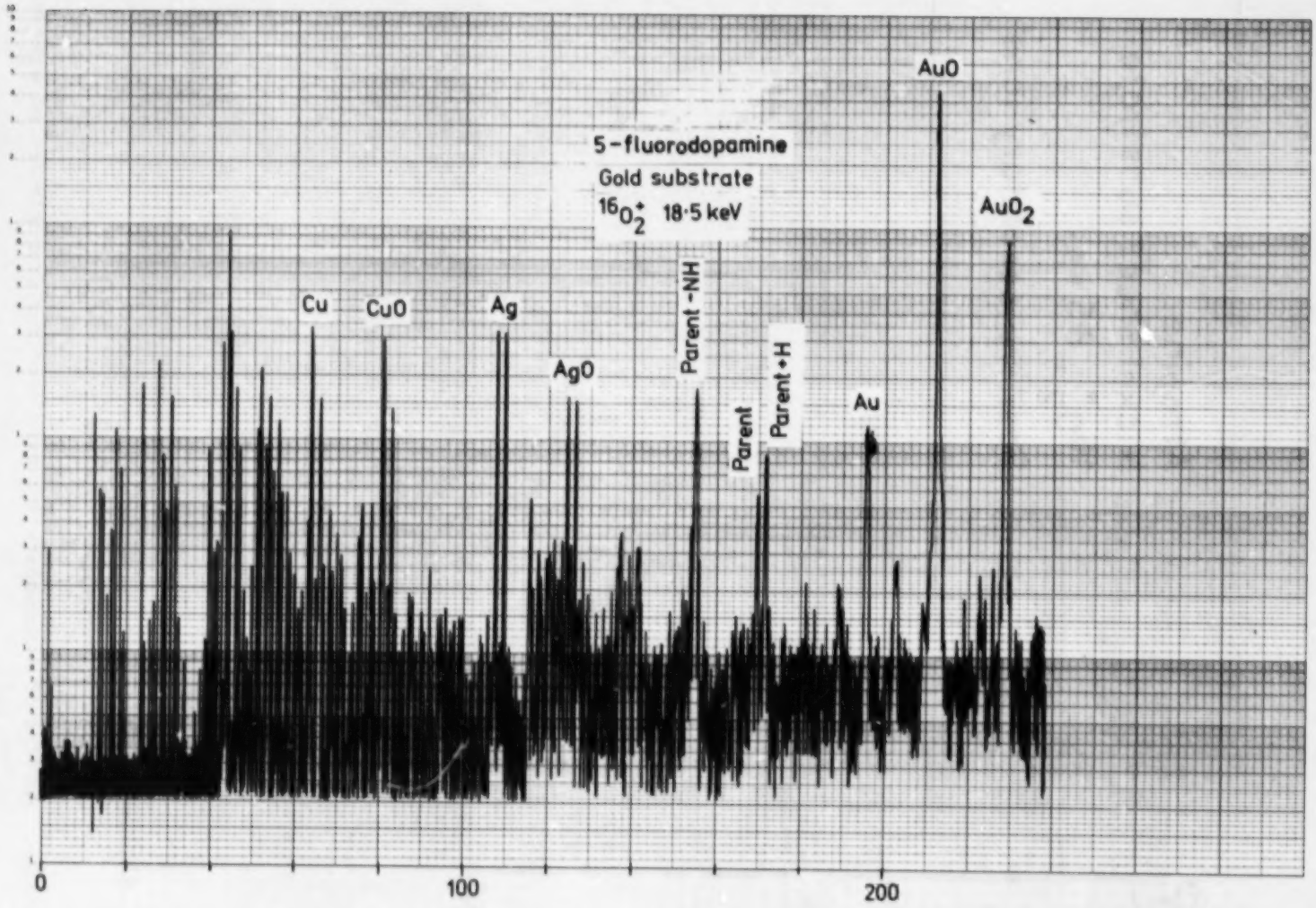

Figure 15. Secondary ion spectrum of fluorodopamine on gold-alloy substrate.

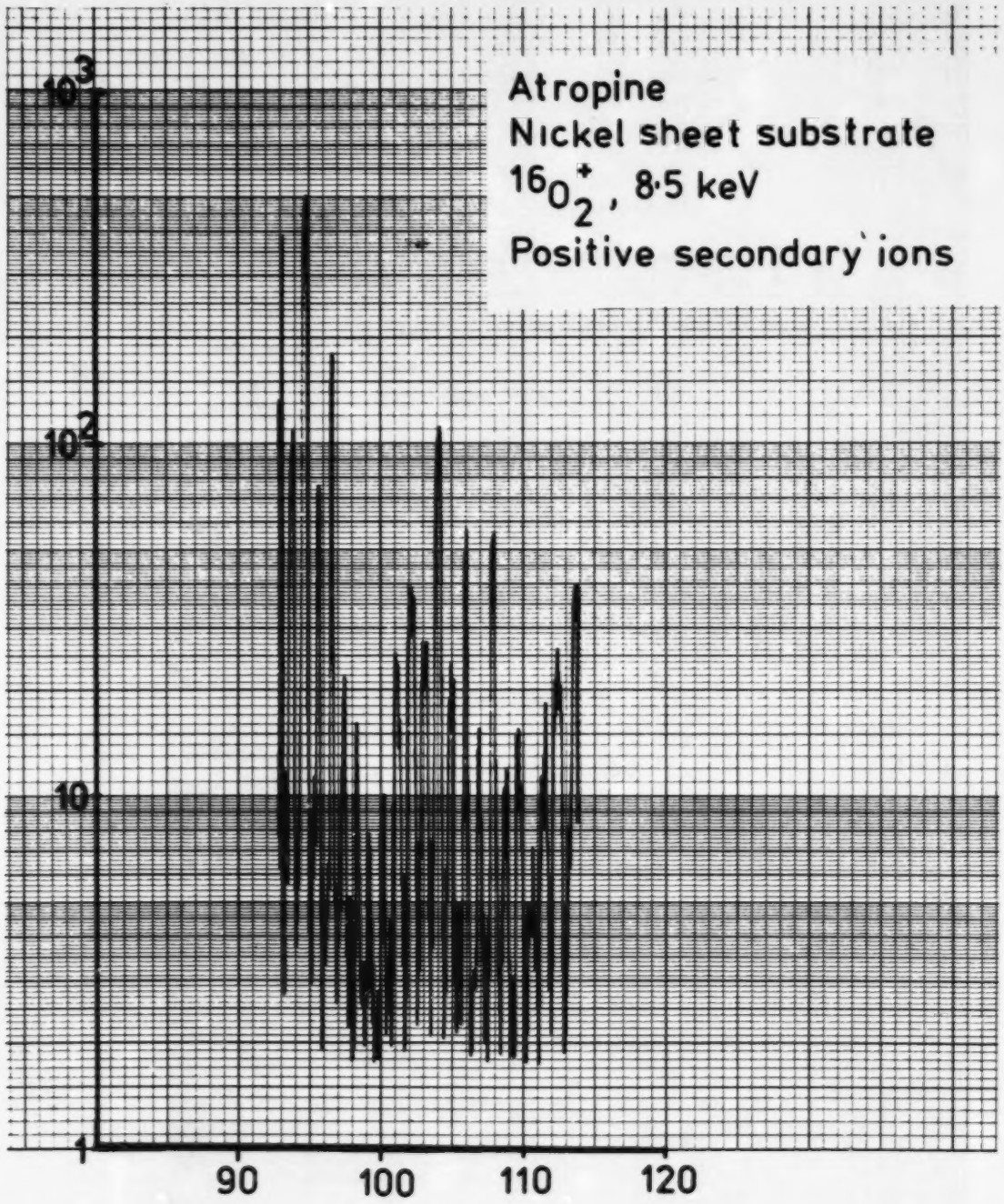

Figure 16. Portion of a secondary ion mass spectrum from glycine on a 20 μm nickel ball.

is maximized for high energy secondary ions, i.e., those sputtered with a kinetic energy above 25 eV. Molecular secondary ions have a probable energy of the order of a few eV, with a narrow energy distribution. Thus, the detection of organic molecular ions in Figures 13 - 16 by ion microprobe suggests that if an instrument were used with enhanced sensitivity in the low kinetic energy region, organic secondary ion mass spectra could be obtained from particles on a routine basis. The ion microscope, a SIMS instrument with adjustable ion optics has the capability to select an energy window to maximize molecular ion collection. This instrument probably offers the best approach to organic mass spectrometry of individual particles.

6. APPLICATIONS OF SIMS TO ENVIRONMENTAL SAMPLES

To demonstrate the feasibility of SIMS for the analysis of environmental samples, several problems have been examined: (1) a study of the capability of SIMS to obtain surface information on particles; (2) a study of elemental depth distributions in particles in SRM 1648 (Urban Particulate Matter); and (3) a study of particles obtained from river sediments.

SURFACE INFORMATION

An example of the capability of obtaining surface information on particles was obtained. In the process of preparing microparticles of known composition to serve as NBS Research Materials in this project, experiments were carried out to convert bulk glasses of known composition into particle form. Filamentary material was created by rapidly pulling threads of molten glass at speeds up to 10 m/s, producing fibers whose diameter ranged as small as 3 μm. Mass spectra were obtained from the fibers under beam conditions chosen to restrict the analysis to a layer within 50 nm of the surface. The spectrum thus obtained (Figure 17) is quite similar to the spectrum of the bulk material (Figure 18), indicating that no surface contamination occurred during the fabrication. Particles were also prepared in spherical form by remelting ground glass particles in an air stream passing through a muffle furnace. In an early experiment, the air stream velocity was too low to prevent the particles from contacting the walls of the furnace. As a result, the surface layer of the particles showed considerable contamination from the boron and sodium components of the ceramic furnace tube, as revealed in a SIMS spectrum (Figure 19). When these particles underwent ion erosion in order to study the interior, spectra similar to the bulk material were obtained. The observation of a thin surface contaminant layer on these artificial particles indicates that useful surface information can be obtained from individual particles.

As an example of a near surface analysis of a single urban particulate, the measured peak intensities in a secondary ion spectrum were converted to compositional values by the sensitivity factor method. The results for this particle analysis are listed in TABLE 3. This particle consisted principally of calcium, sodium, aluminum, silicon, and iron. Minor elements include boron, magnesium, potassium, titanium, chromium, nickel and lead. Lithium and barium were observed at trace levels.

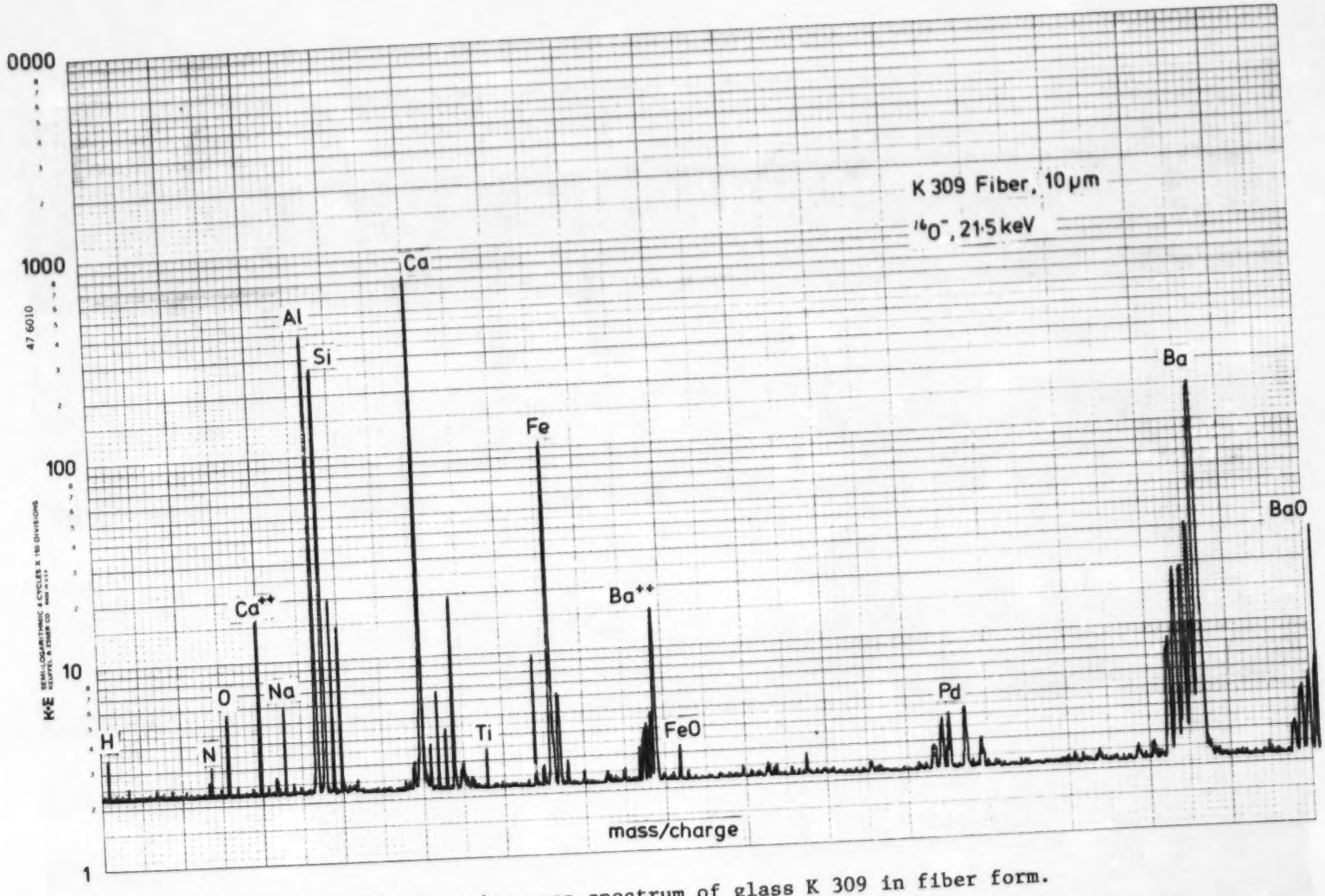

Figure 17. Secondary ion mass spectrum of glass K 309 in fiber form.

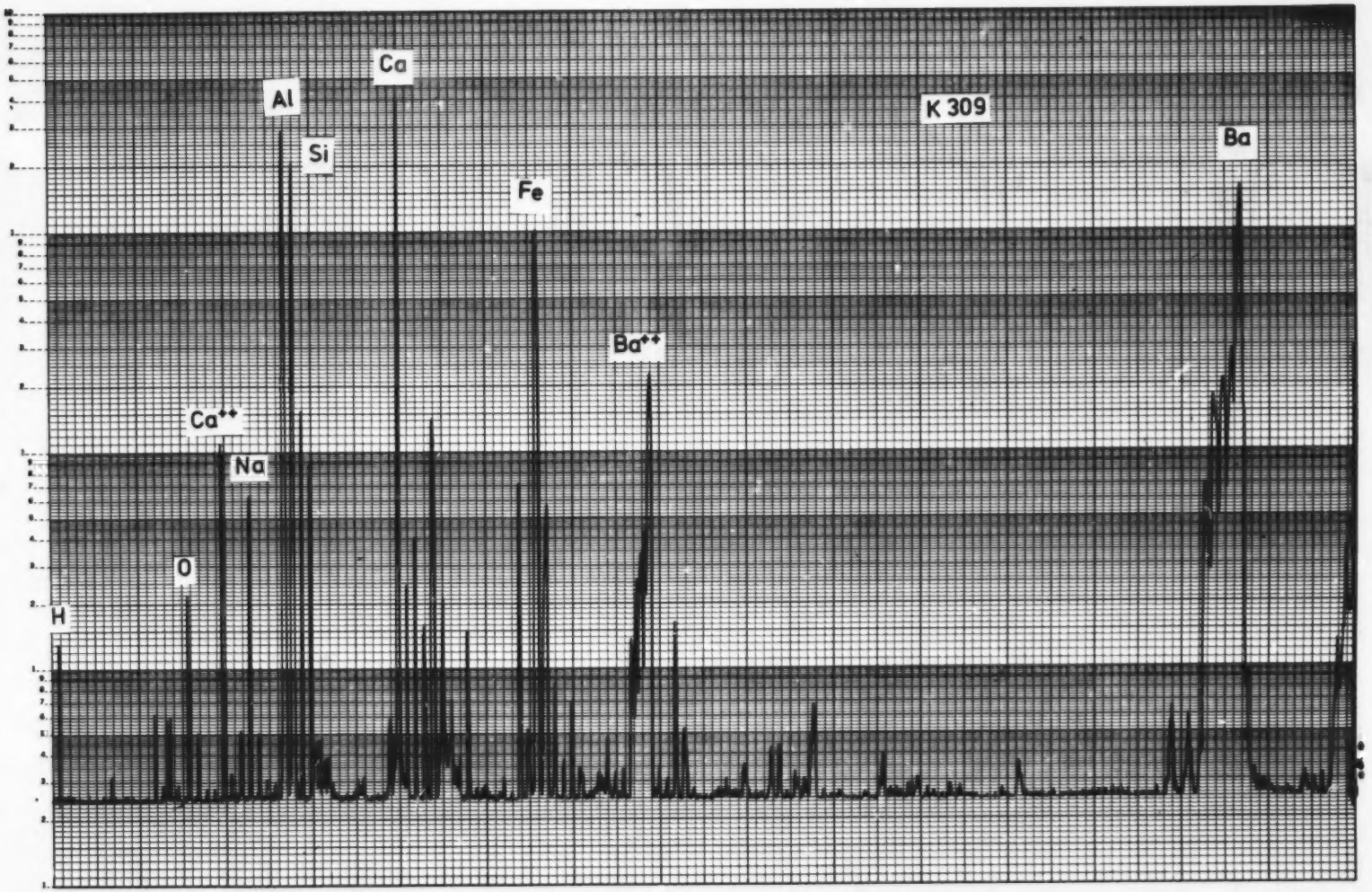

Figure 18. Secondary ion mass spectrum of glass K 309 in bulk form.

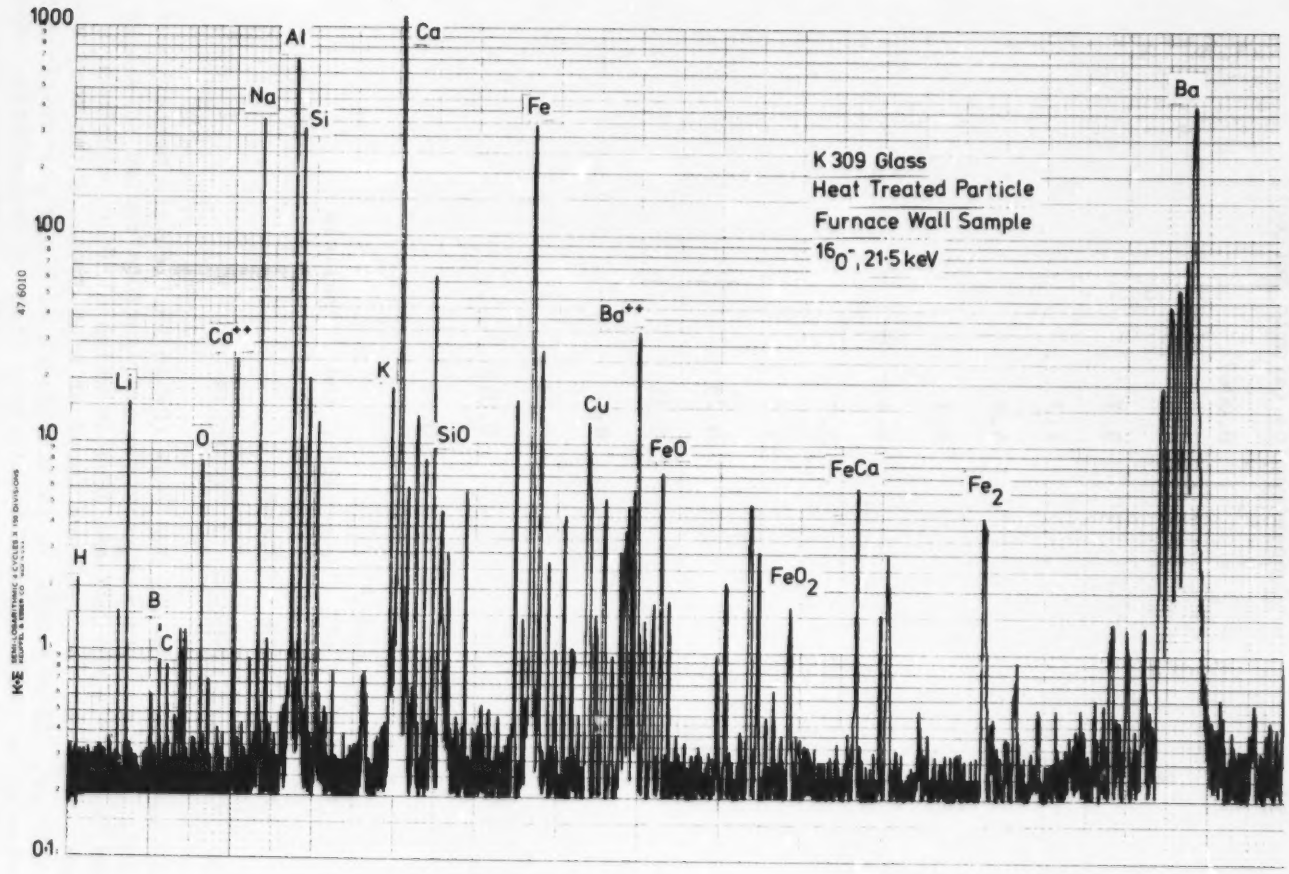

Figure 19. Secondary ion spectrum of K 309 spherical glass particle collected from wall of remelt furnace.

TABLE 3. ANALYSIS OF THE SURFACE LAYER OF AN URBAN ENVIRONMENTAL PARTICULATE WITH RELATIVE SENSITIVITY FACTORS DERIVED FROM NBS GLASSES

Element	Concentration (atomic percent)
Li	0.0067
B	0.62
Na	3.3
Mg	1.3
Al	4.0
Si	6.1
P	2.1
K	1.7
Ca	12.8
Ti	0.25
Cr	0.21
Fe	6.8
Ni	0.42
Ba	0.012
Pb	0.28

The sum of all the metallic and methalloid elements was assumed to be 40 atomic percent; balance - oxygen.

DEPTH PROFILING OF LAYERED ATMOSPHERIC PARTICLES

Individual particles from NBS SRM 1648 (Urban Particulate Matter) were examined by SIMS. Spectra obtained from the near-surface region show a range of compositions (e.g., Figures 20a and 20b) in which silicon, aluminum, calcium, sodium, chlorine, and iron are found at high levels which very from particle to particle. This result is in accordance with our observations of individual particles in this material by electron probe microanalysis. Minor elements observed in individual particles include lithium, fluorine, boron, barium, and lead.

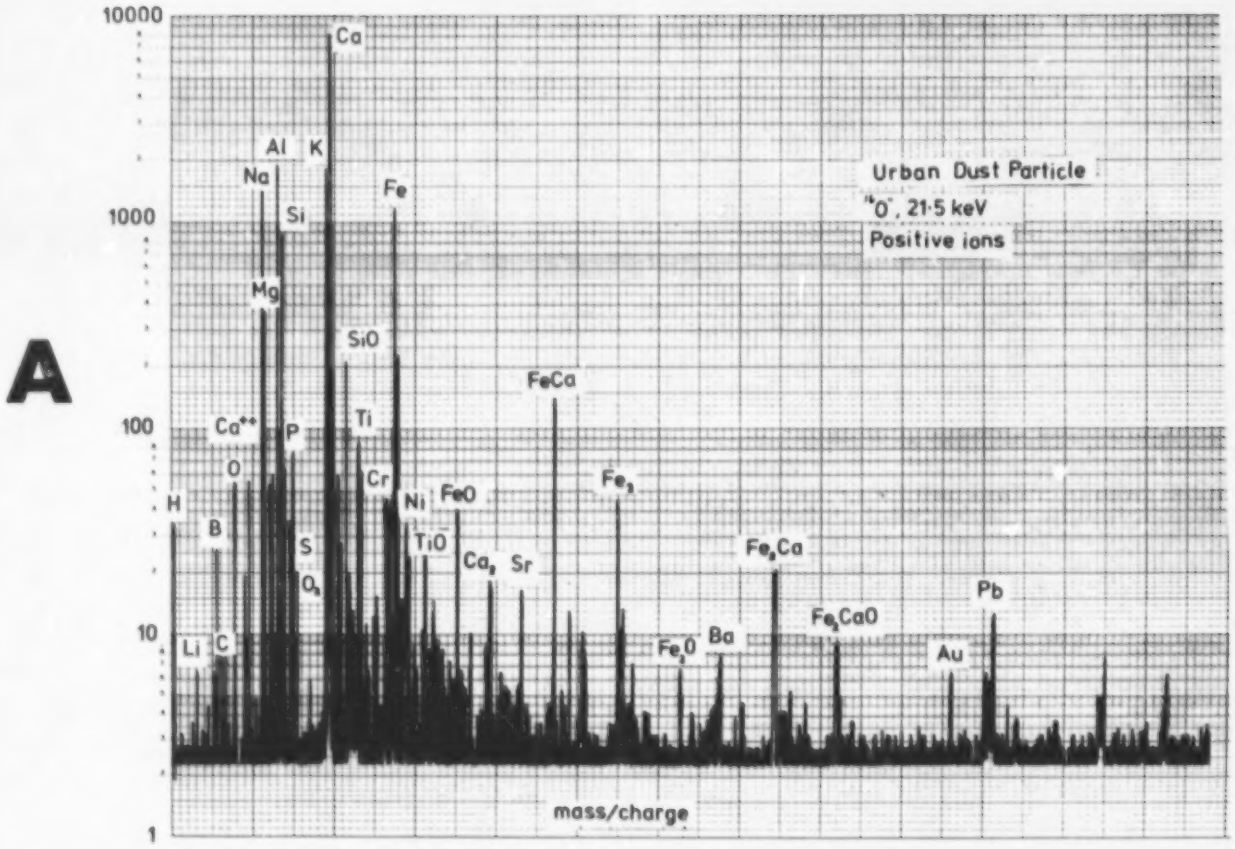

Figure 20. Secondary ion mass spectra of an individual particle from SRM 1648 (Urban Air Particulate). (a) Positive secondary ions.

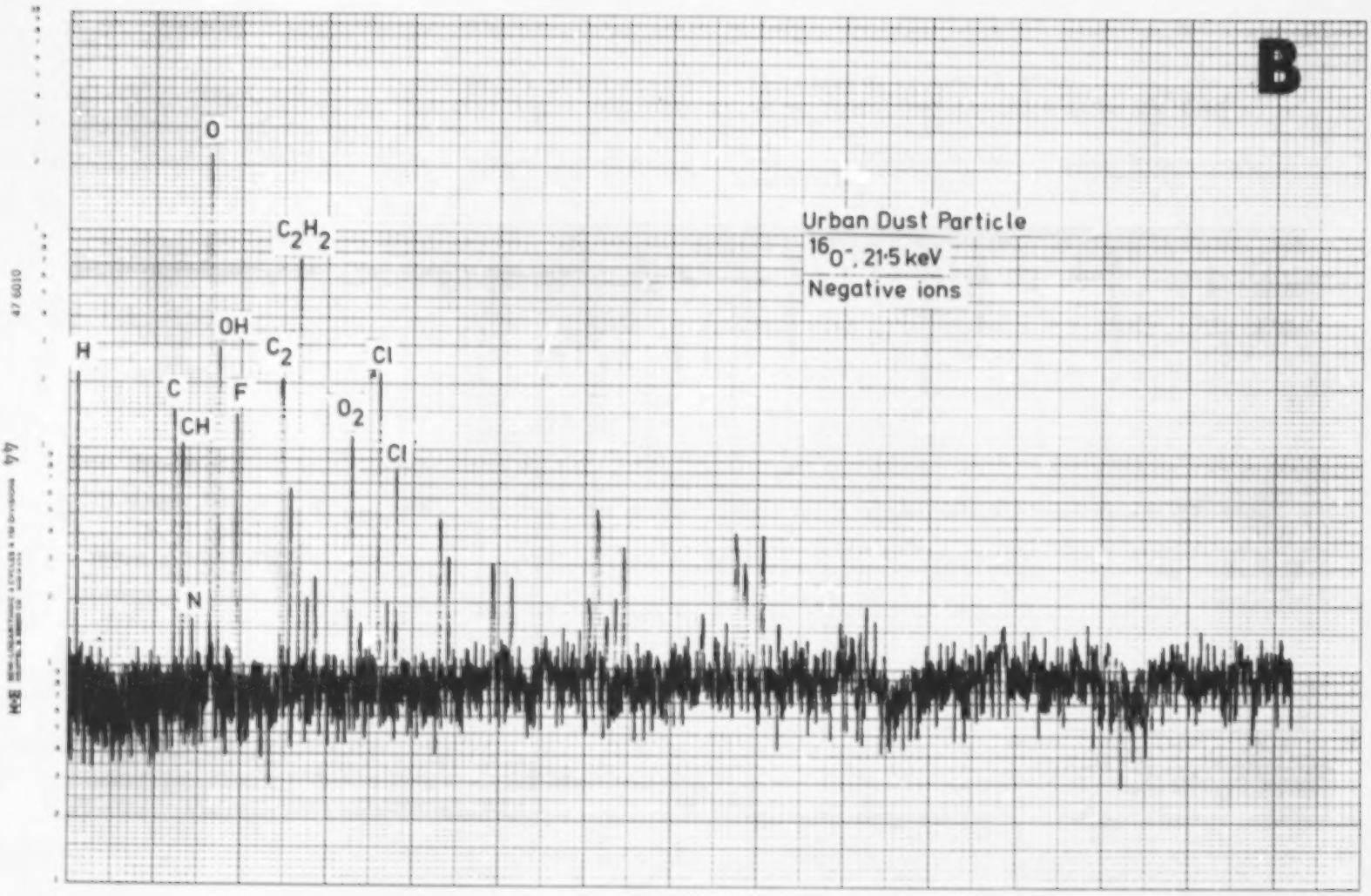

Figure 20. Secondary ion mass spectra of an individual particle from SRM 1648 (Urban Air Particulate). (b) Negative secondary ions.

Depth profiles were recorded on selected individual particles in the size range 5 - 10 μm. Figure 21 shows a multielement depth profile obtained by manual tuning of the secondary spectrometer to record the intensities of seven elements as a function of depth. The intensities of aluminum, iron, barium, lithium, lead, and boron were normalized with the signal for silicon to minimize matrix effects. A complex behavior is observed in this specimen for a number of elements. Initially, all elements except aluminum increase with depth. After approximately 0.5 μm of the particle was removed, the barium and lead levels dropped significantly, before recovering to a nearly stable level at a depth of 2 μm. The range of the barium and lead levels over the depth scale studied is more than two orders of magnitude, with the interior depleted in these heavy elements relative to the surface. This result was observed frequently in a collection of about 20 particles which were studied in this manner (24). The result was recently confirmed on a state-of-the-art ion microprobe which had a computer-controlled secondary ion spectrometer for rapid peak switching for the recording of multi-element depth profiles. Two particles studied Figures 22a and 22b showed decreasing levels of barium and lead toward the interior while the silicon signal remained remarkably constant.

In the UAP sample as a whole, bulk chemical analysis reveals a lead level of about 0.65 weight percent. The result that at least a fraction of the particles contain enhanced surface levels of lead suggests that the biological significance of the lead content of the sample may be substantially greater than the bulk analysis suggests. Thus, when these urban air pollution particles are ingested, the outer layers of the particles will be the first to interact with body tissues. It is specifically these outer layers in which the heavy metals in the sample are concentrated. Thus, the amount of heavy metals which can be absorbed into the tissue locally near a particle may be much greater than the average analysis value for the whole sample would indicate.

The practicality of using SIMS depth profiling to study particles is chiefly limited by the degree of automation available on the instrument, particularly with regard to multiplexing secondary ion signals. In the NBS ARL ion microprobe mass analyzer, peaks of interest must be tuned manually, making the recording of multi-element depth profiles tedious. Moreover, the time factor causes a loss of depth resolution. In the new CAMECA IMS-3F ion microscope, the state of automation is such that depth profiles such as Figures 22a and 22b are rapidly obtained in a straightforward manner.

STUDIES OF STREAM SEDIMENTS

Individual particles from a series of stream sediments were examined from three locations: New York Harbor, Indiana Harbor Canal, and the Ohio River. Surface spectra from representative individual particles in these samples are shown in Figures 23a, 23b, and 23c. Again, complex particle compositions are observed, with high levels of silicon, carbon, aluminum, potassium, calcium, and iron. Minor levels of lithium, boron, sodium, titanium, manganese, strontium, barium, and lead have also been observed.

Elemental depth profiles for iron, carbon, aluminum, and silicon in separate particles from New York Harbor are shown in Figures 24a, 24b, 24c,

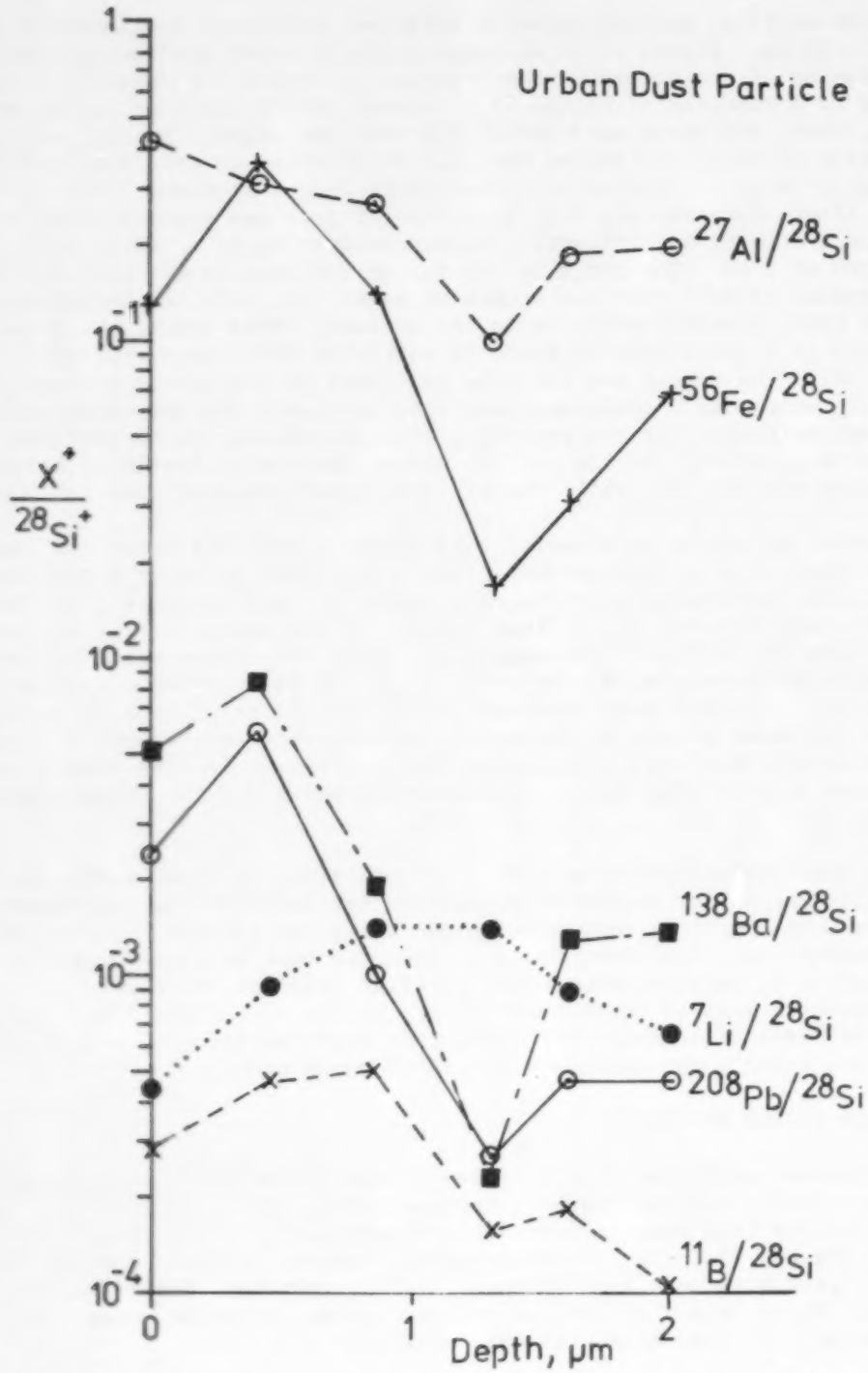

Figure 21. Multi-element depth profile obtained by manual scanning. Sample: individual particle of SRM 1648 (Urban Air Particulate) with a diameter of approximately 10 micrometers.

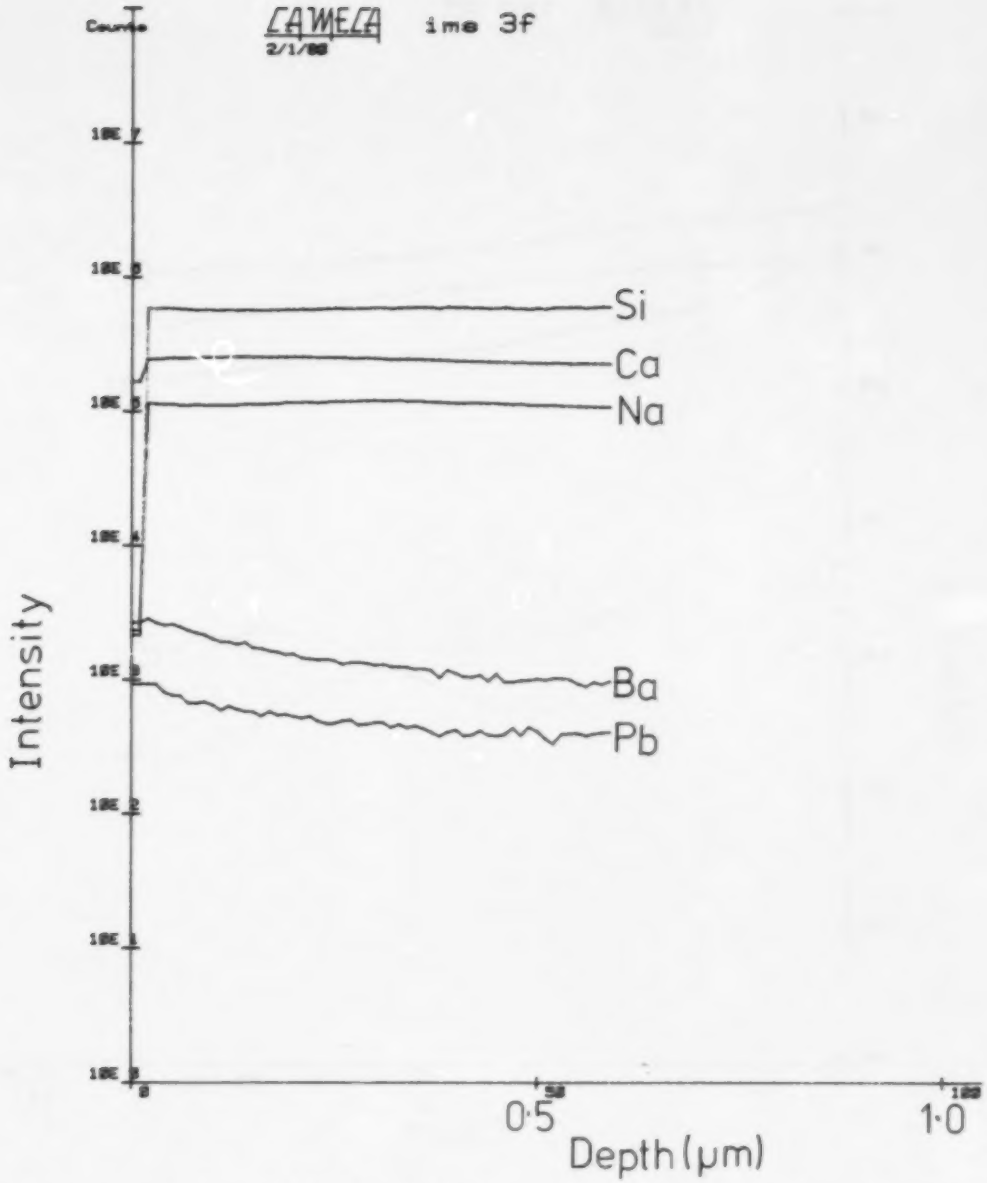

Figure 22. Multi-element depth profiles of individual particles from SRM 1648 obtained with automated ion microscope (a) Particle size 5 micrometers.

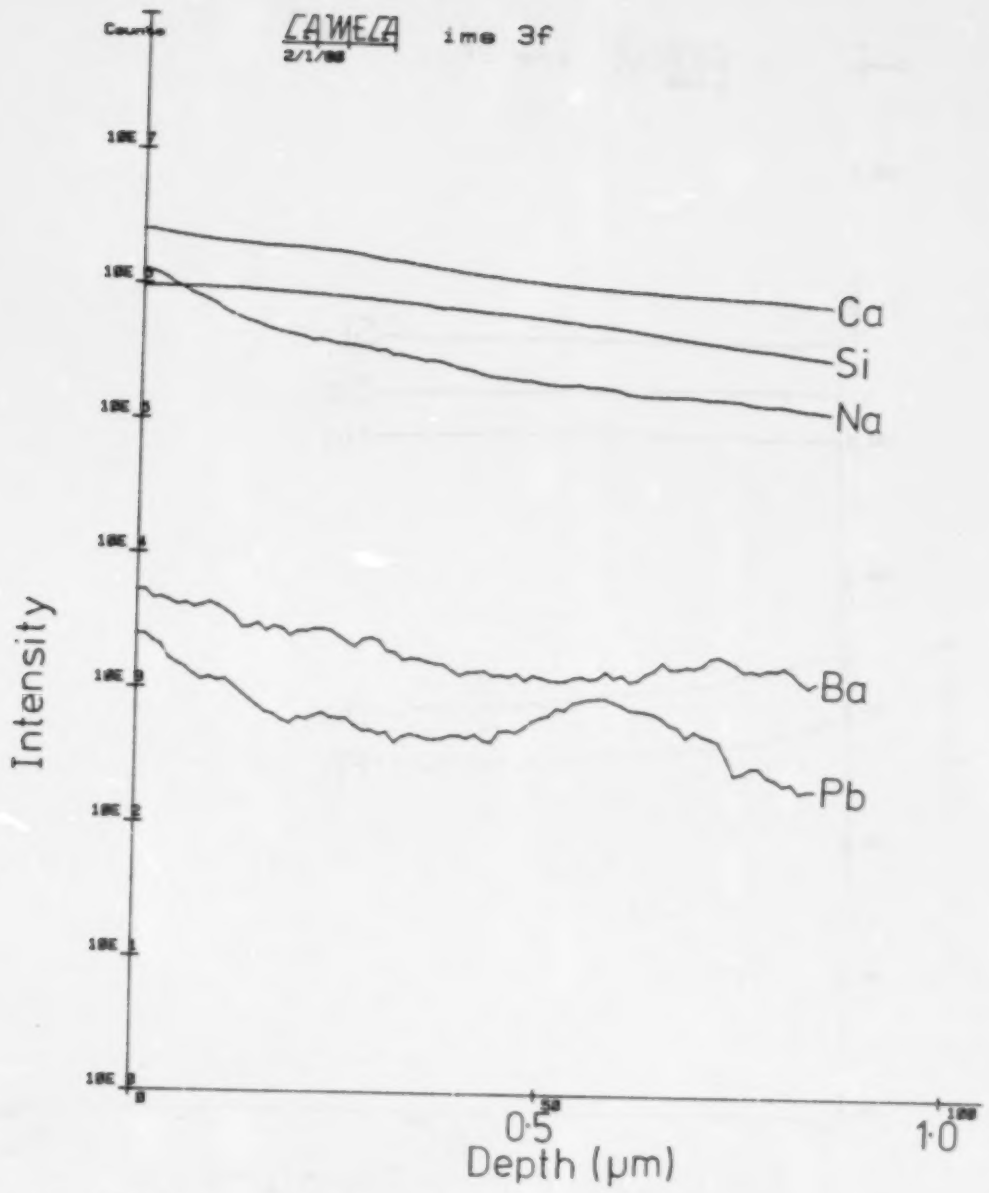

Figure 22. Multi-element depth profiles of individual particles from SRM 1648 obtained with automated ion microscope (b) Particle size 4 micrometers.

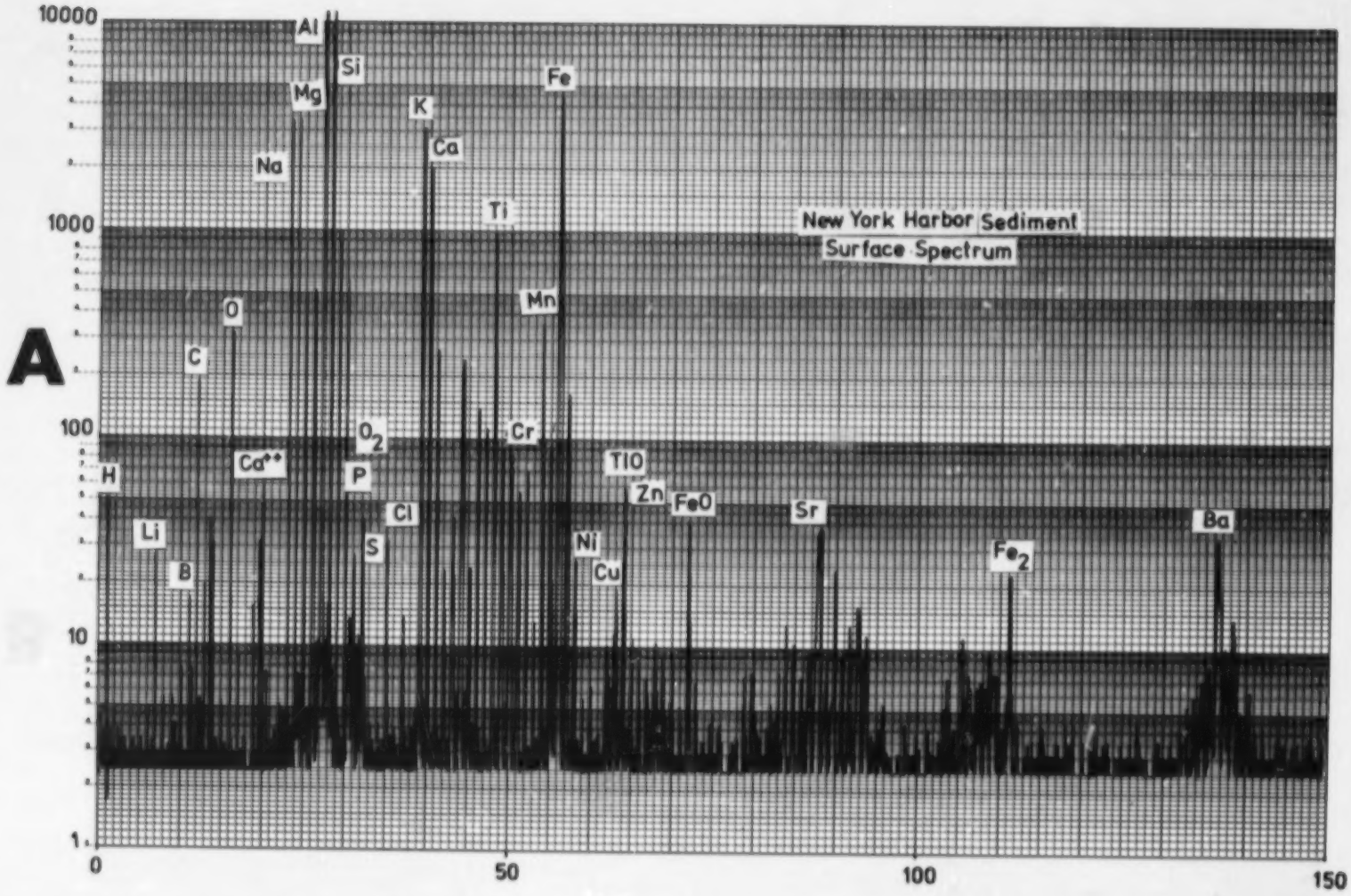

Figure 23. Near-surface secondary ion spectra obtained from single 10 micrometer sized sediment particles (a) New York Harbor.

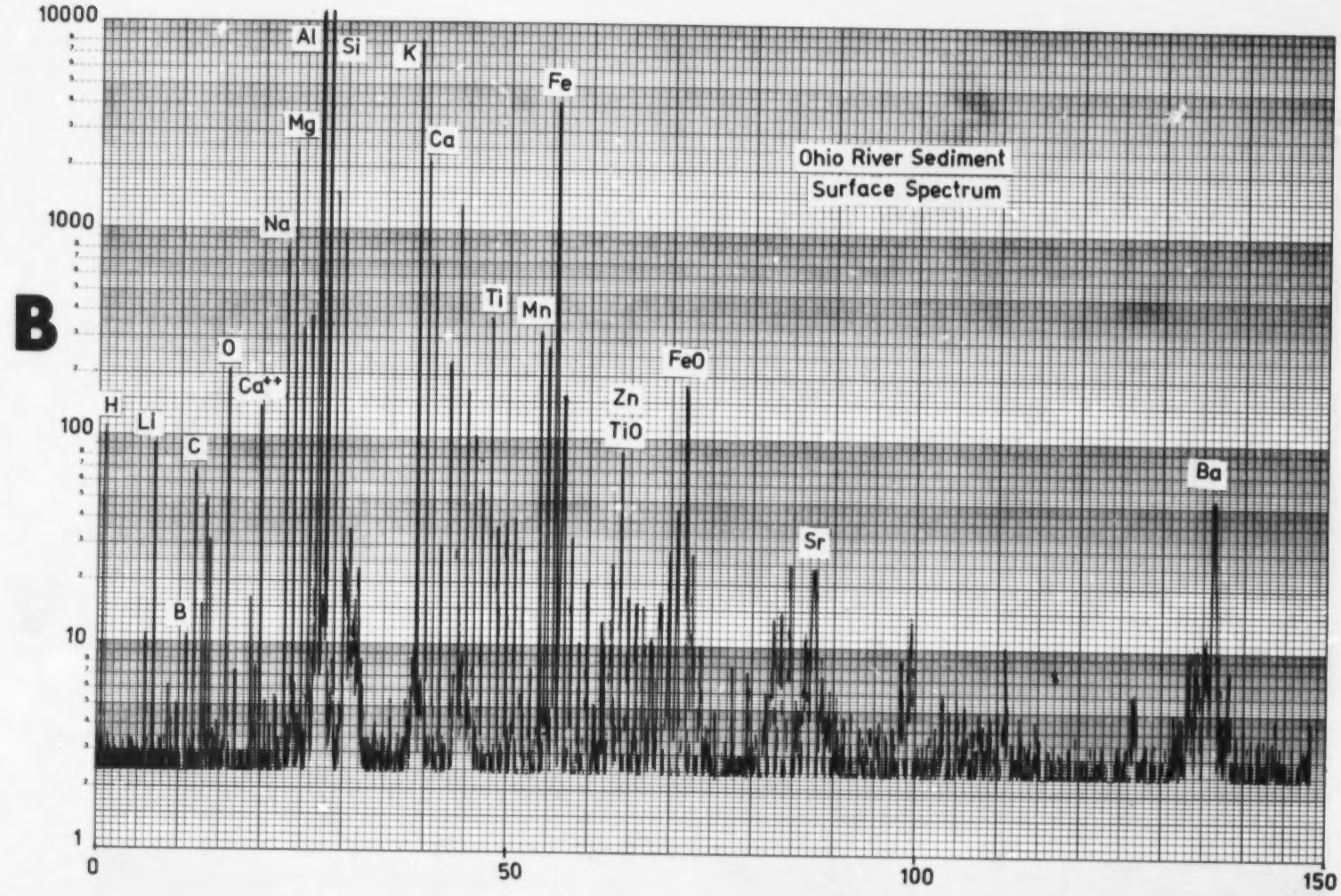

Figure 23. Near-surface secondary ion spectra obtained from single 10 micrometer sized sediment particles (b) Ohio River.

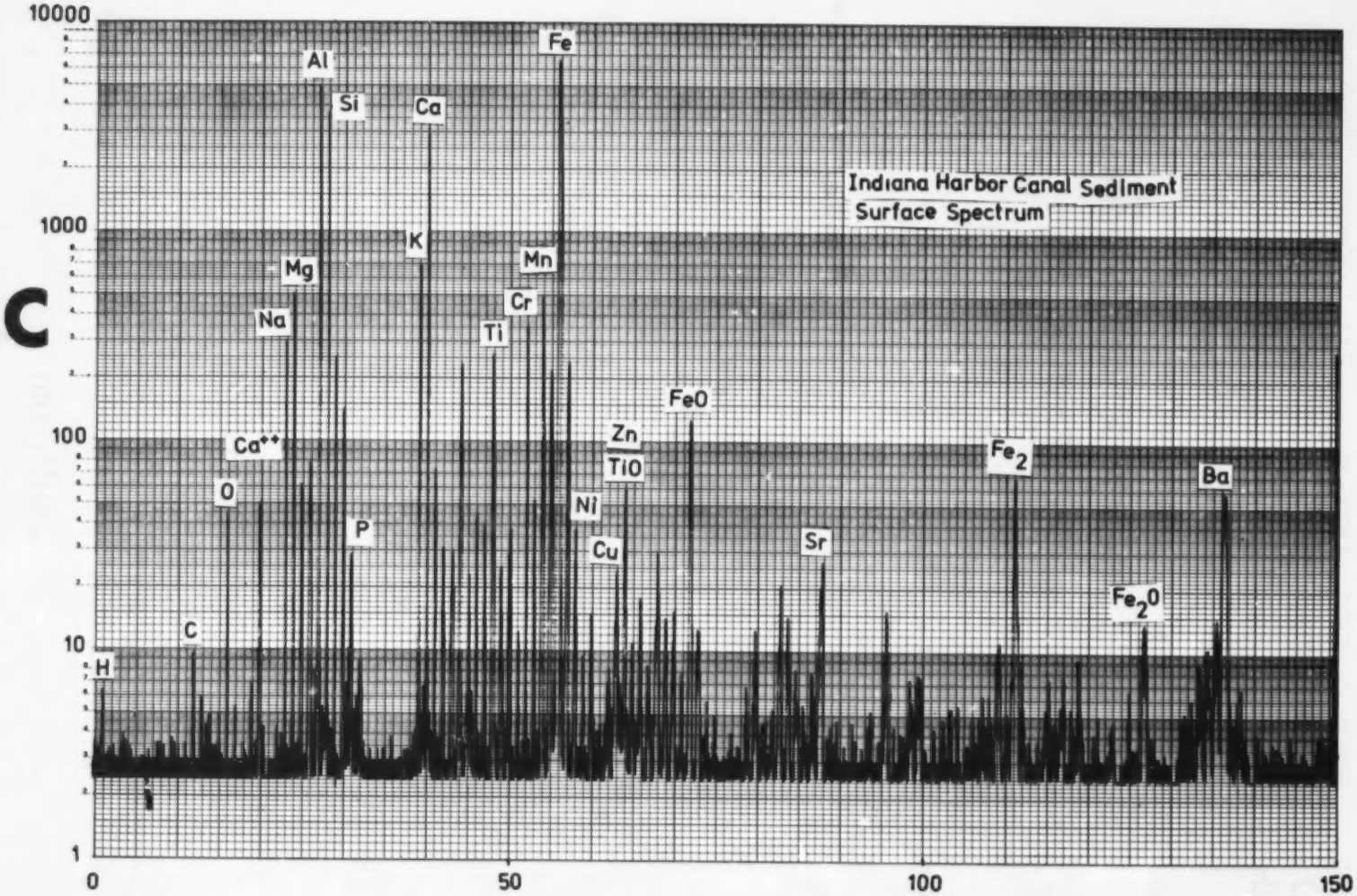

Figure 23. Near-surface secondary ion spectra obtained from single 10 micrometer sized sediment particles (c) Indiana Harbor Canal.

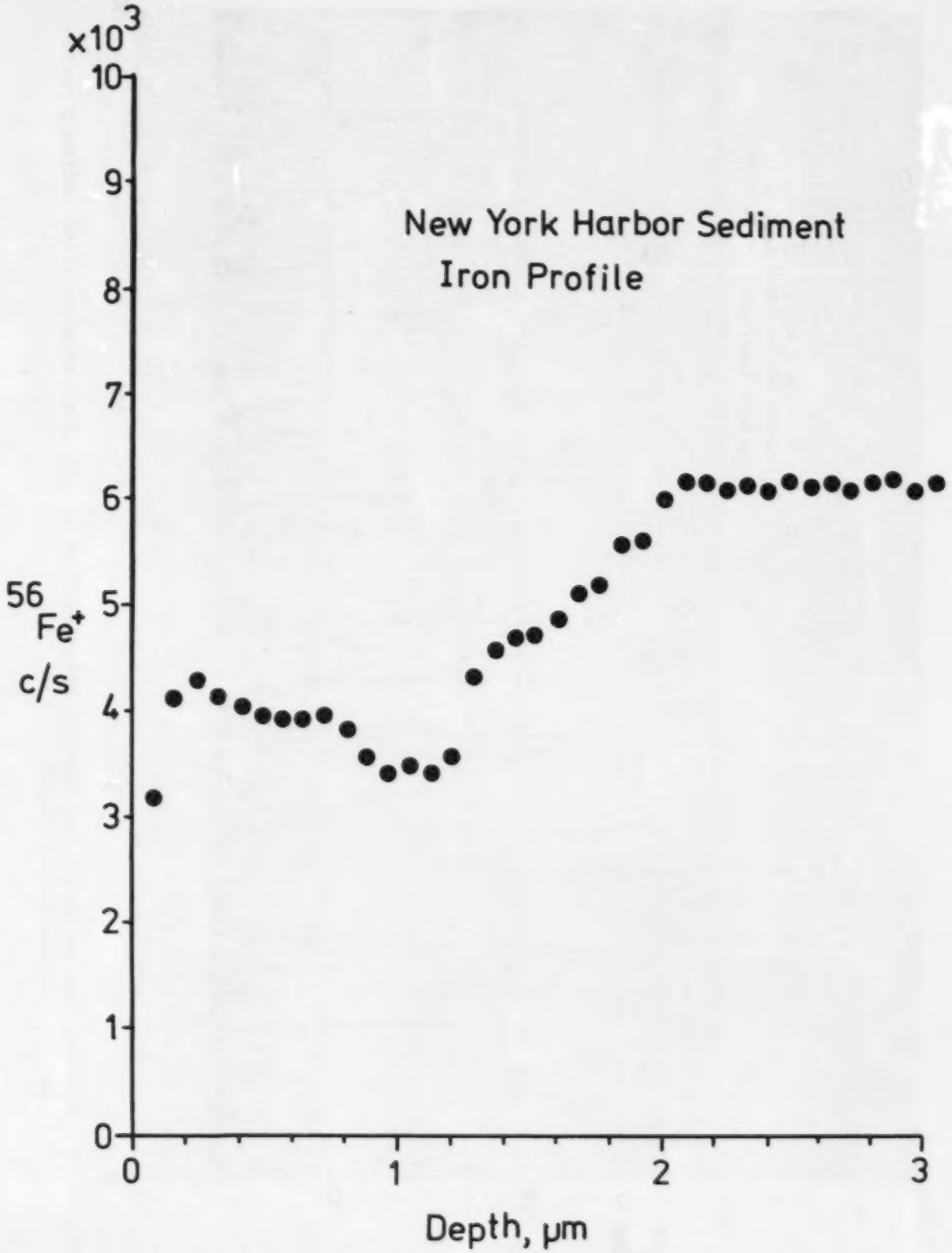

Figure 24. Single element depth profiles obtained from different individual particles from New York Harbor (a) Iron.

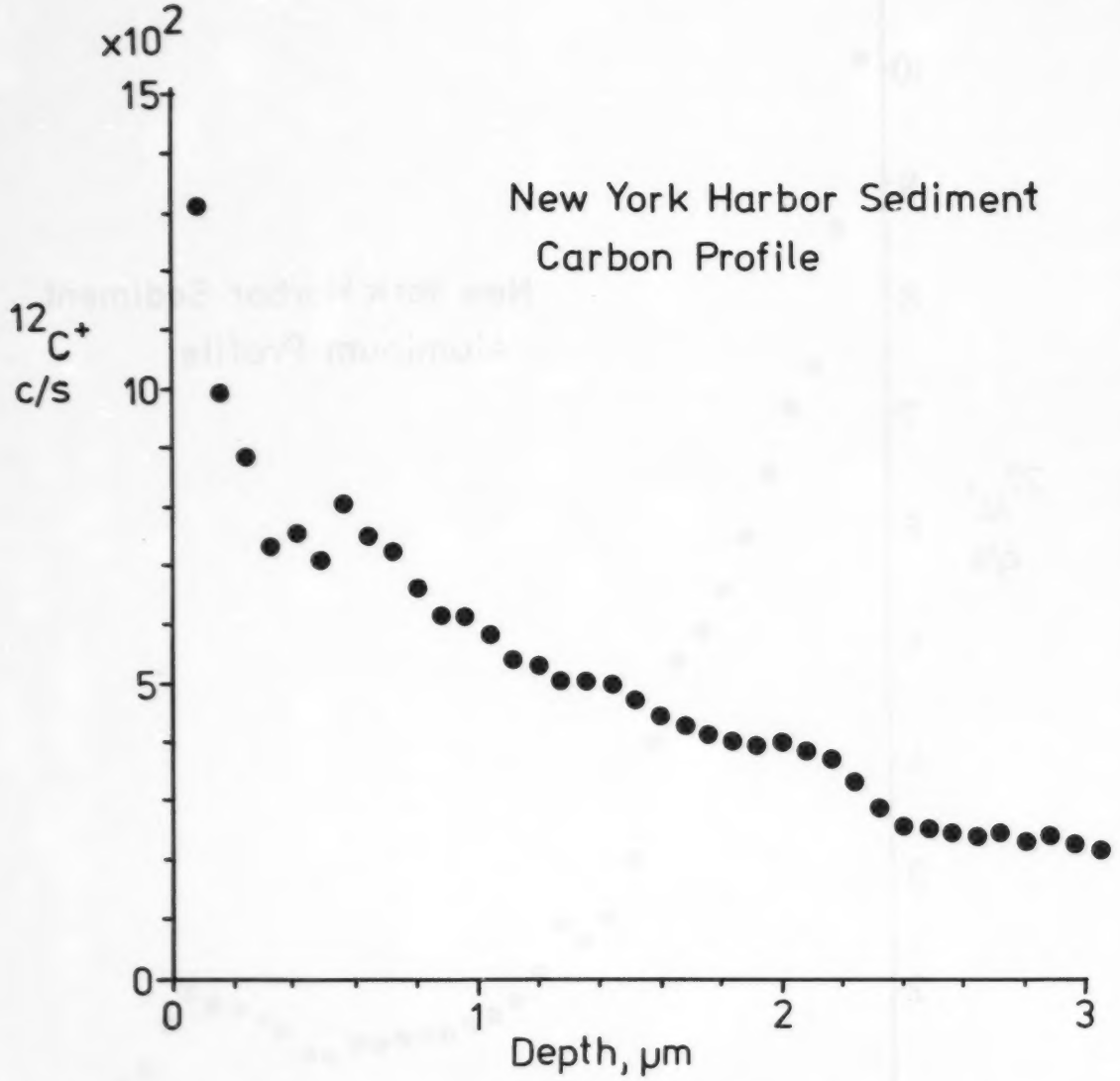

Figure 24. Single element depth profiles obtained from different individual particles from New York Harbor (b) Carbon.

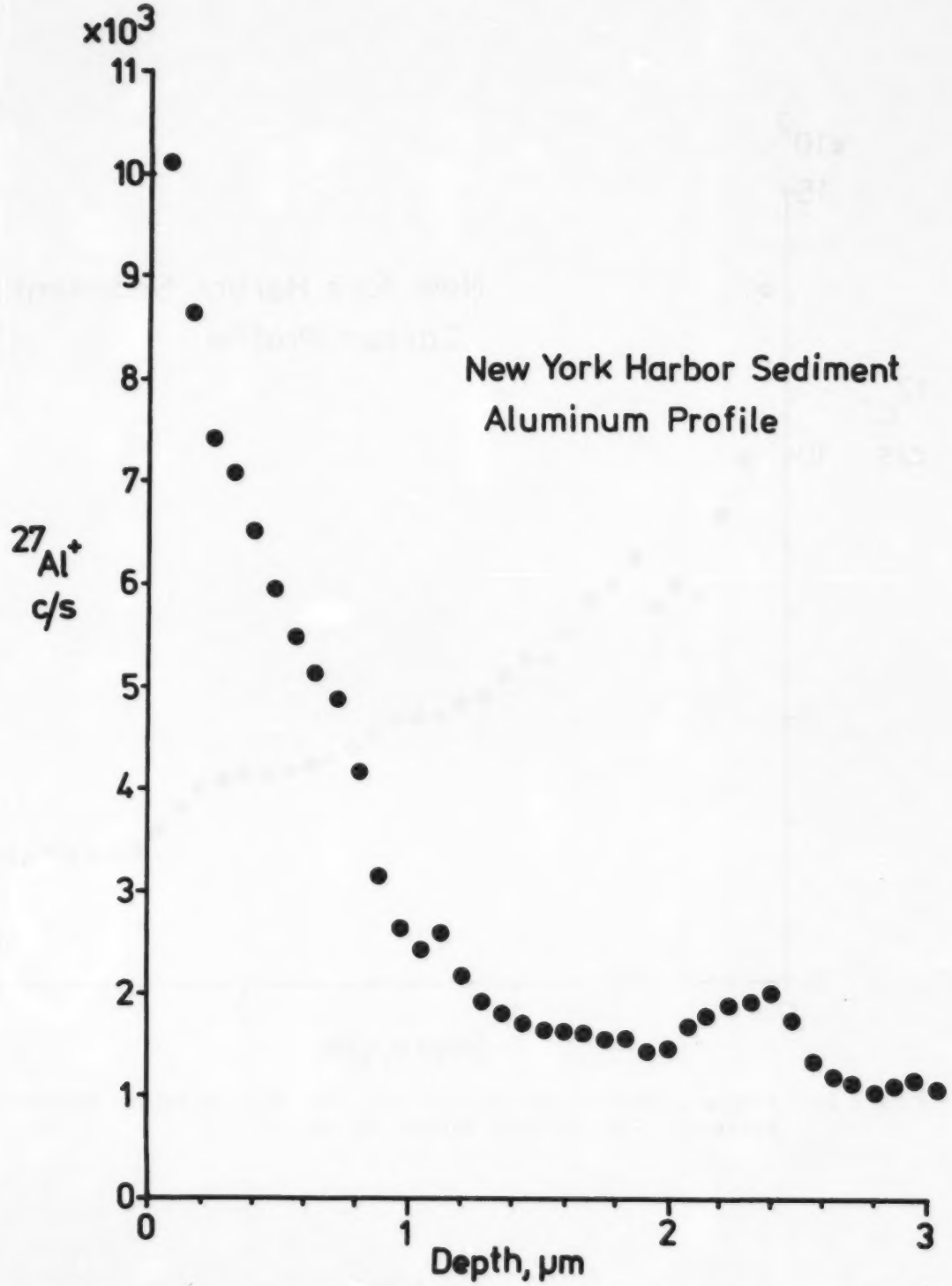

Figure 24. Single element depth profiles obtained from different individual particles from New York Harbor (c) Aluminum.

and 24d. In this case, the secondary mass spectrometer was tuned to a specific peak and the signals were measured at a constant time interval. In the resulting profiles, features where the composition varies with a depth resolution of 0.1 μm or less can be observed, demonstrating the depth resolution which can be obtained by the SIMS technique. In a modern ion microscope with rapid peak switching, this depth resolution could be achieved even when multi-element depth profiles are measured.

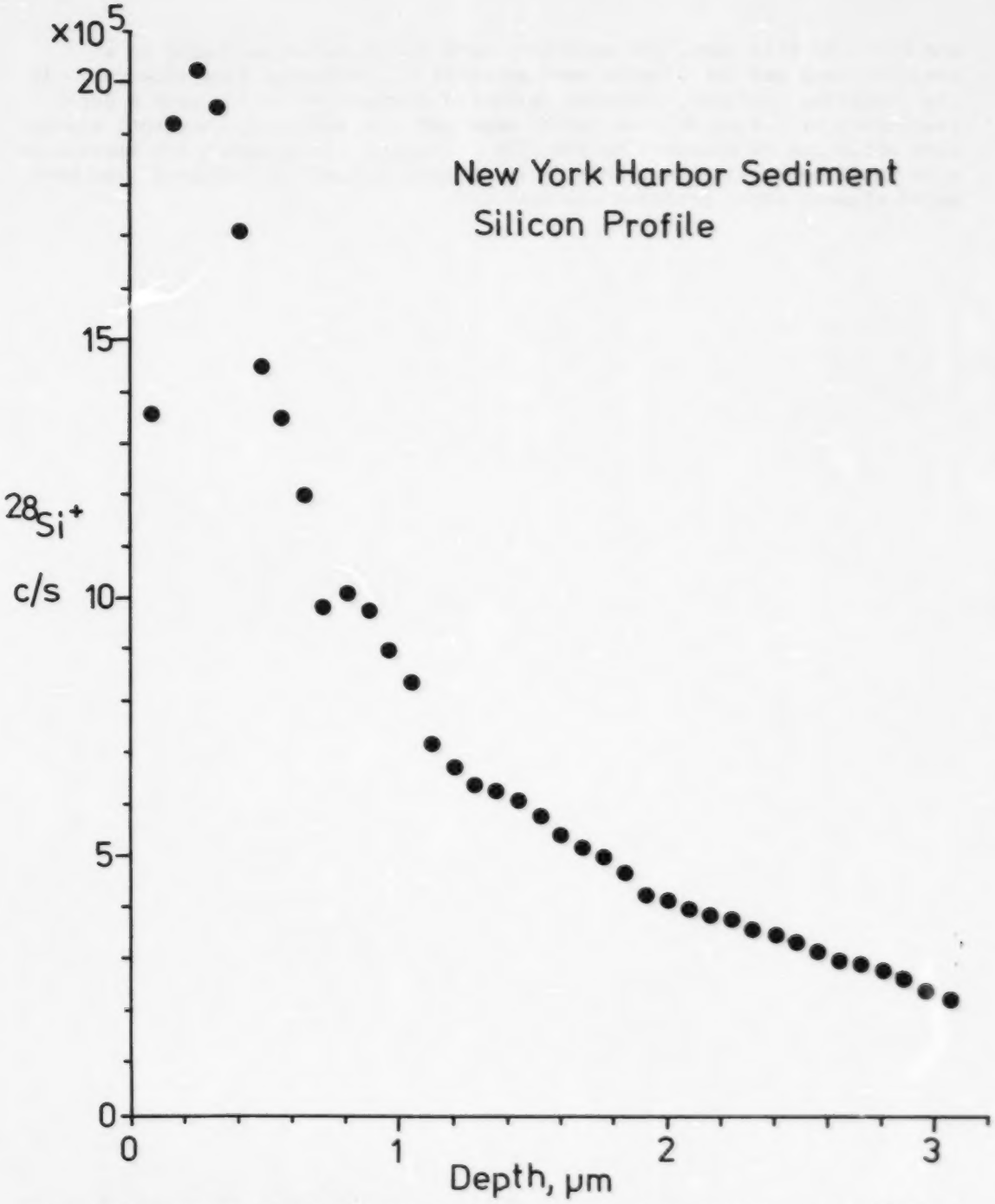

Figure 24. Single element depth profiles obtained from different individual particles from New York Harbor (d) Silicon.

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